SURFACE-DIRECTED SPINODAL DECOMPOSITION

LATTICE MODEL VERSUS GINZBURG-LANDAU THEORY

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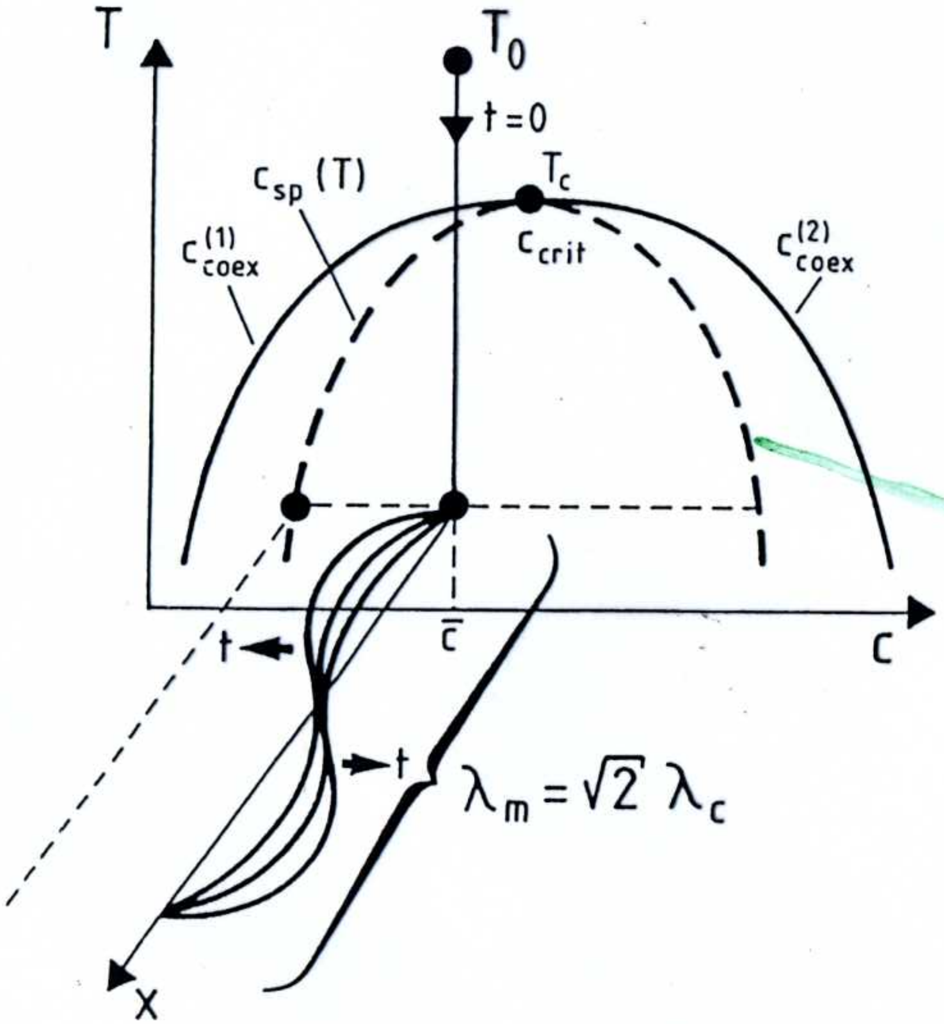
Sanjay PURI, Harry L. FRISCH (✝2007)

SPINODAL DECOMPOSITION



unstable binary mixture:
miscibility gap

quenching experiment

Cahn-Hilliard 1958

Cahn 1961

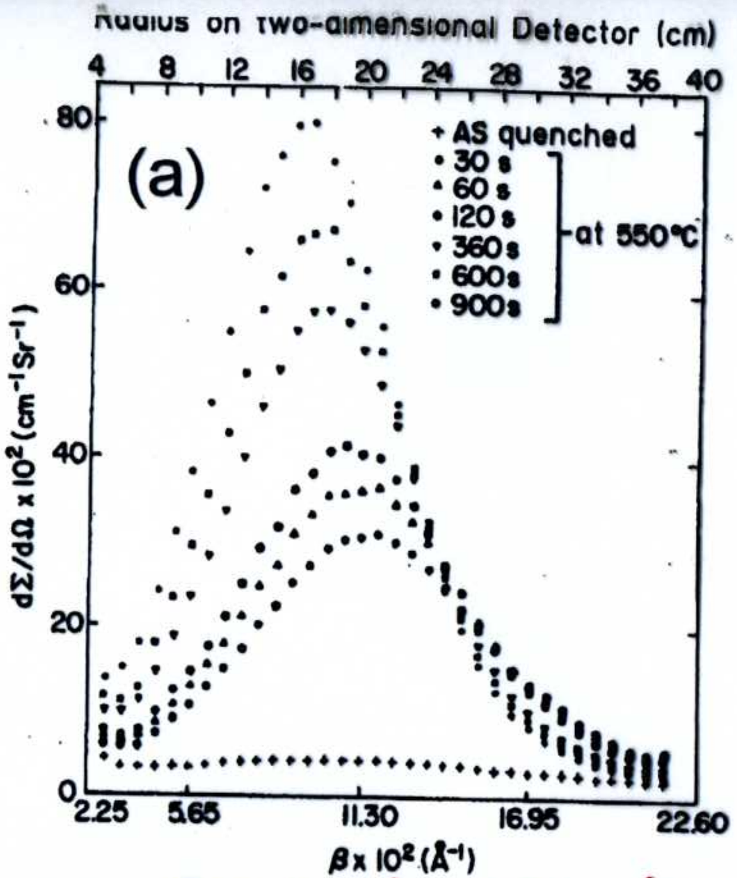
spinodal

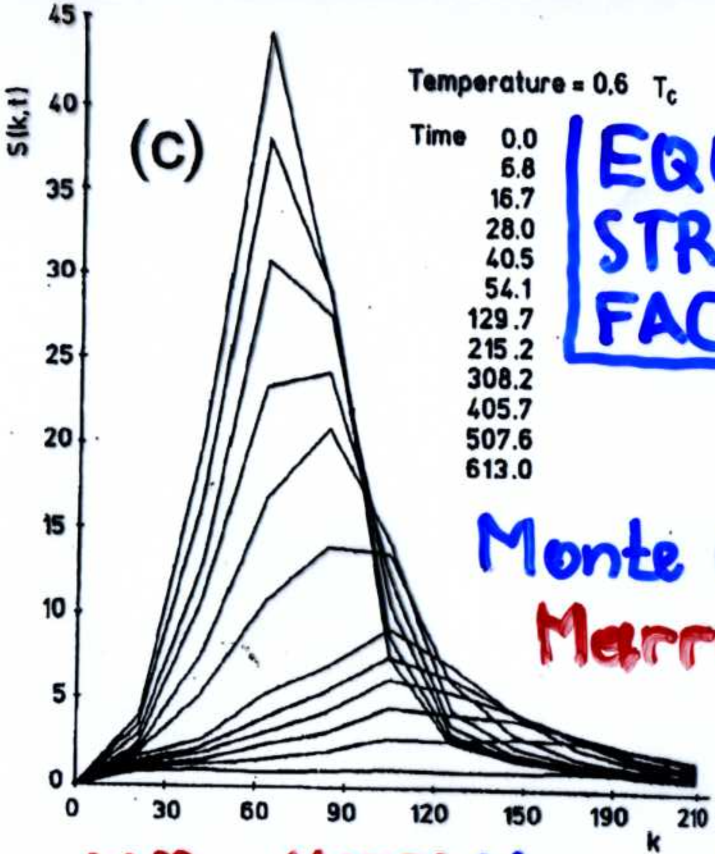
concentration

unstable wavepacket : growing
concentration waves

Au-Pt alloy

Singhal et al. (1978)





EQUAL-TIME STRUCTURE FACTOR

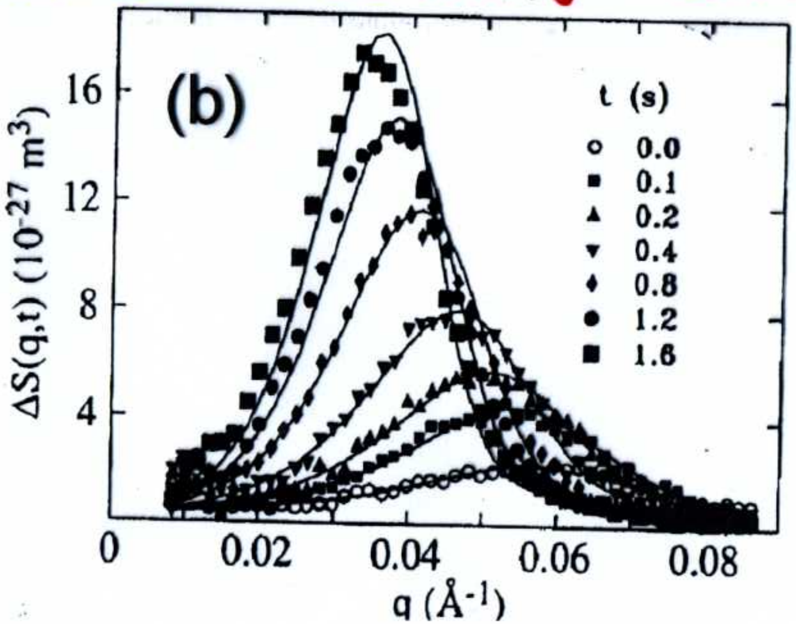
Monte Carlo (1975)

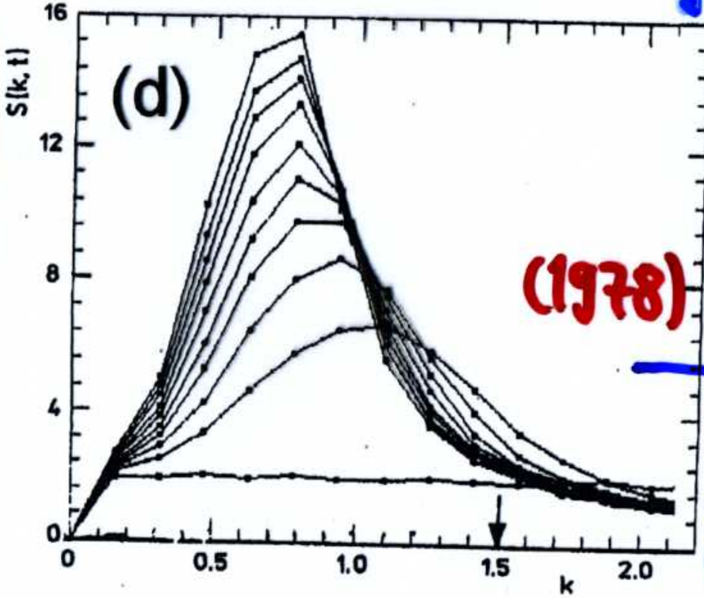
Marro et al.

Curves: fit to Langer-Baron-Miller (1975) theory (nonlinear extension of Cahn-Hilliard th.)

Al-Zn alloy

Mainville et al. (1997)





(1978) Milchev et al.

→ numerical solution of discretized C-H theory

- no exponential growth of equal-time structure factor $S(q,t)$ with time t after the quench

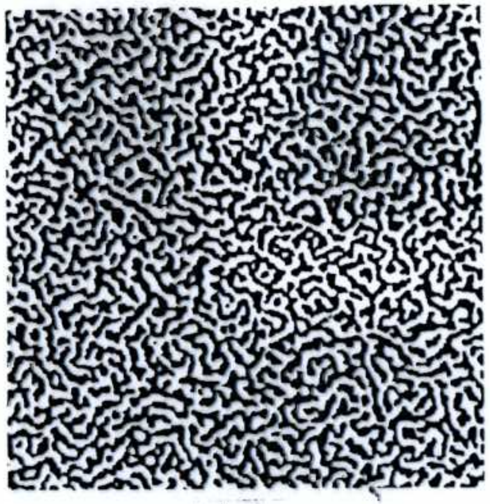
- concentration fluctuations of initial state $\Rightarrow$ NONLINEAR EFFECTS important $\Rightarrow$ COARSENING

$q_m(t) \propto \ell^{-1}(t) \propto t^{-1/3}$

Lifshitz-Slyozov (1961)

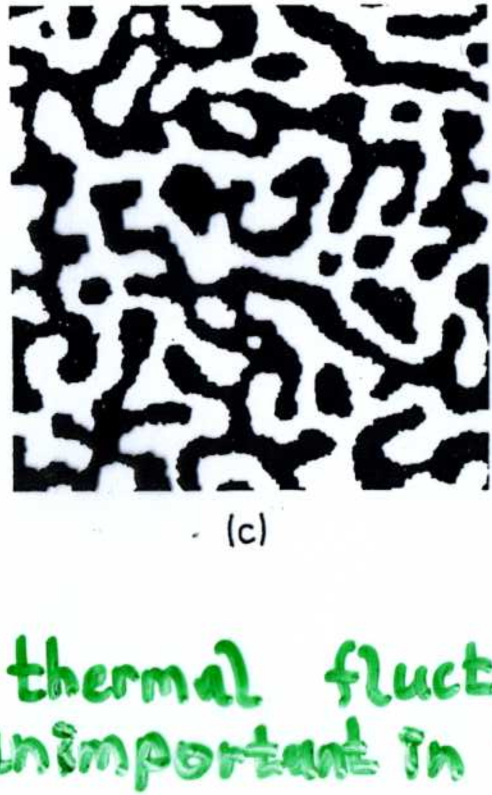
SCALING

$S(q,t) = [\ell(t)]^d \tilde{S}[q\ell(t)]$



(a)

(b)



(c)

Amar et al. (1988)

Monte Carlo

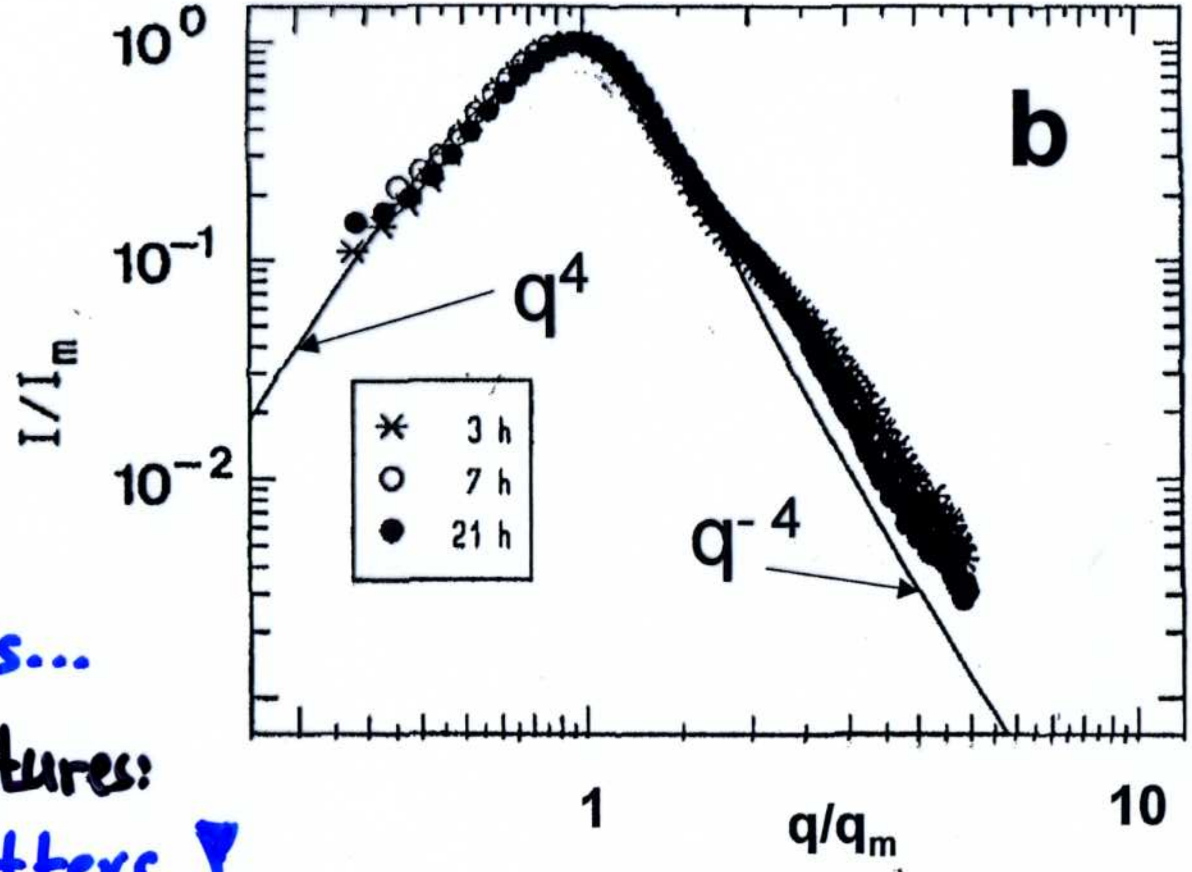
thermal fluctuations unimportant in late stages!

- Scaling function $\tilde{S}[q\ell(t)]$?
- Dependence of $\ell(t)$, $\tilde{S}$ on volume fraction ϕ of new phase ?

PROBLEMS ! data (Al-Ag): Langmayr et al. (1992)
model fct: Fratzl + Lebowitz (1989)

- Crossover from SPINODAL DECOMPOSITION to NUCLEATION

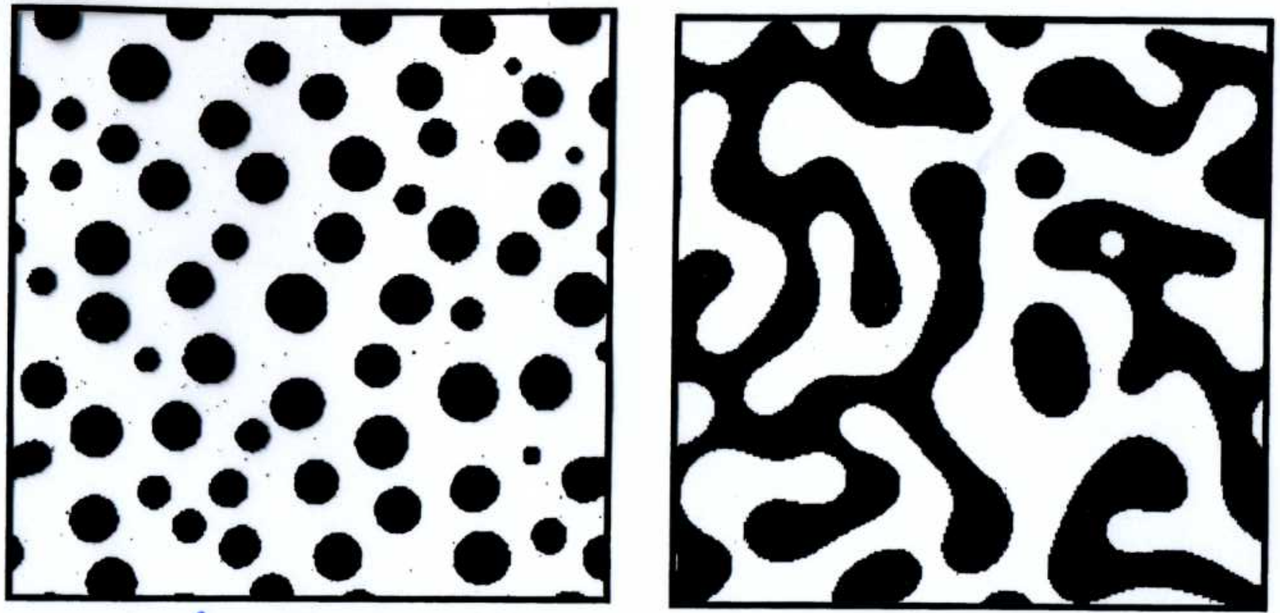
SPINODAL is MEAN-FIELD-ARTEFACT for systems with short-range forces...



- Fluid binary mixtures: hydrodynamics matters !

numerical solution of the nonlinear Cahn-Hilliard (Ginzburg-Landau) equation

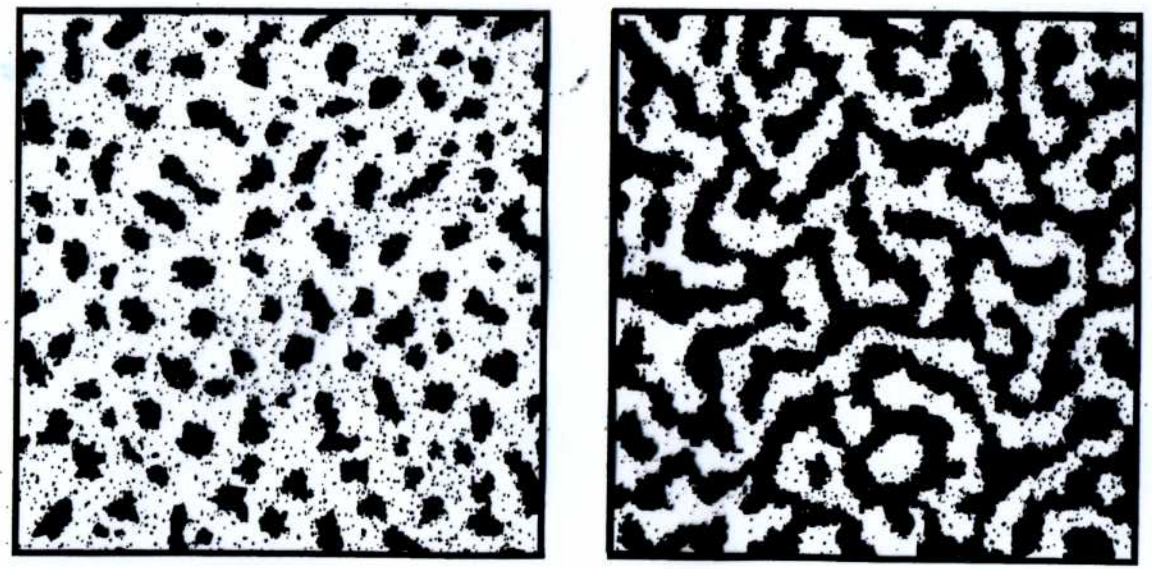
Rogers + Desai (1989)



$\phi = 0.21$ $\phi = 0.5$

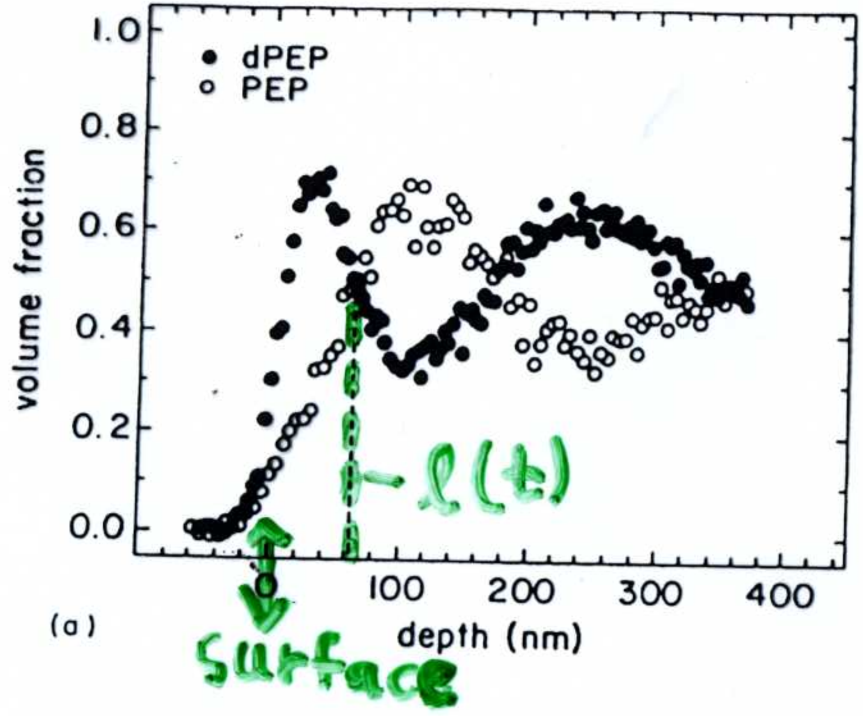
Kawasaki spin-exchange kinetic Ising model

MONTE CARLO



Phase separation of binary mixtures confined in thin films: SURFACE-DIRECTED SPINODAL DECOMPOSITION

Krausch et al. (1993)

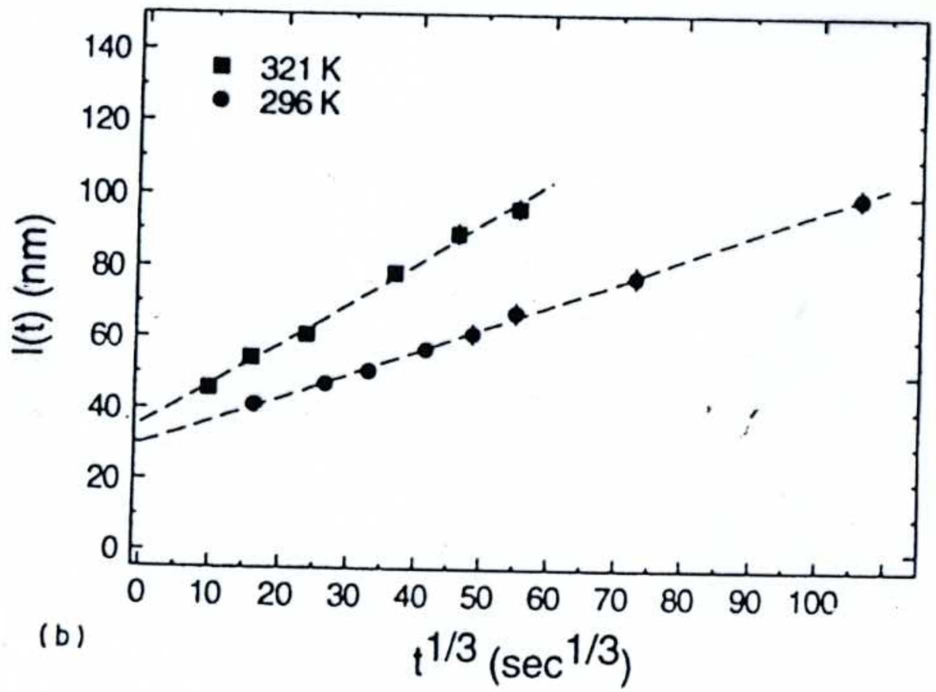


damped concentration wave due to enrichment of one component preferred by surface

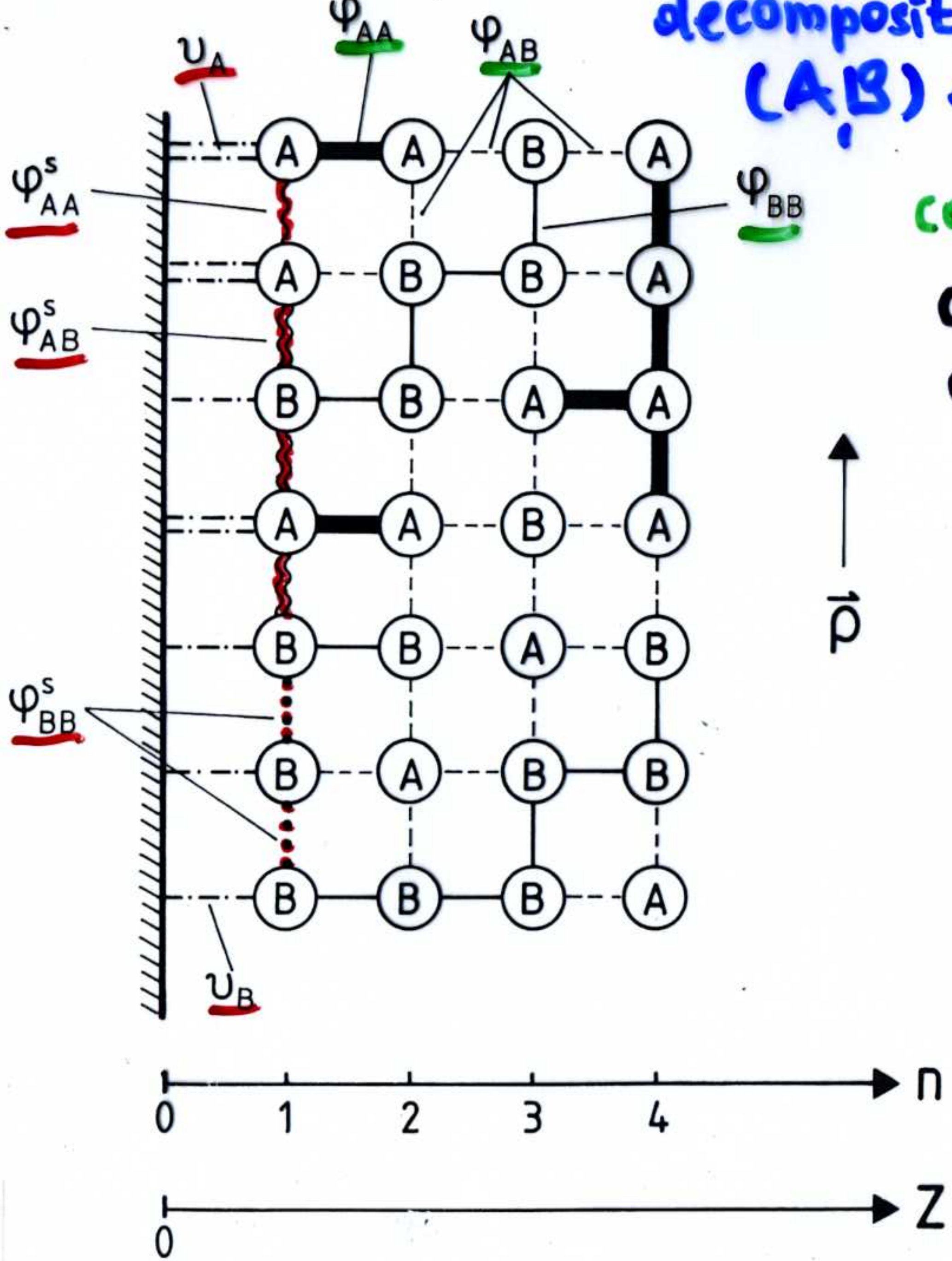
Sometimes $\ell(t) \propto t^{1/3}$

although fluid mixture

(highly viscous polymer mixture)

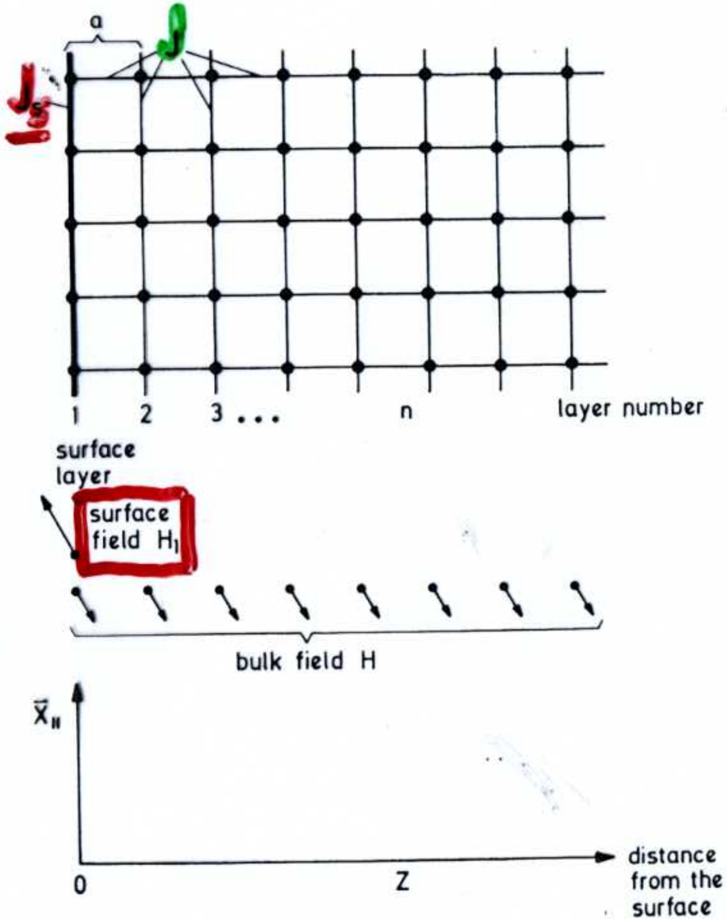


Theoretical description of surface effects on spinodal decomposition in solid (crystalline) binary (A,B) alloys



concentration variables → Ising spins

$$c_i = 1 \Leftrightarrow A \rightarrow S_i = +1$$
$$c_i = 0 \Leftrightarrow B \rightarrow S_i = -1$$



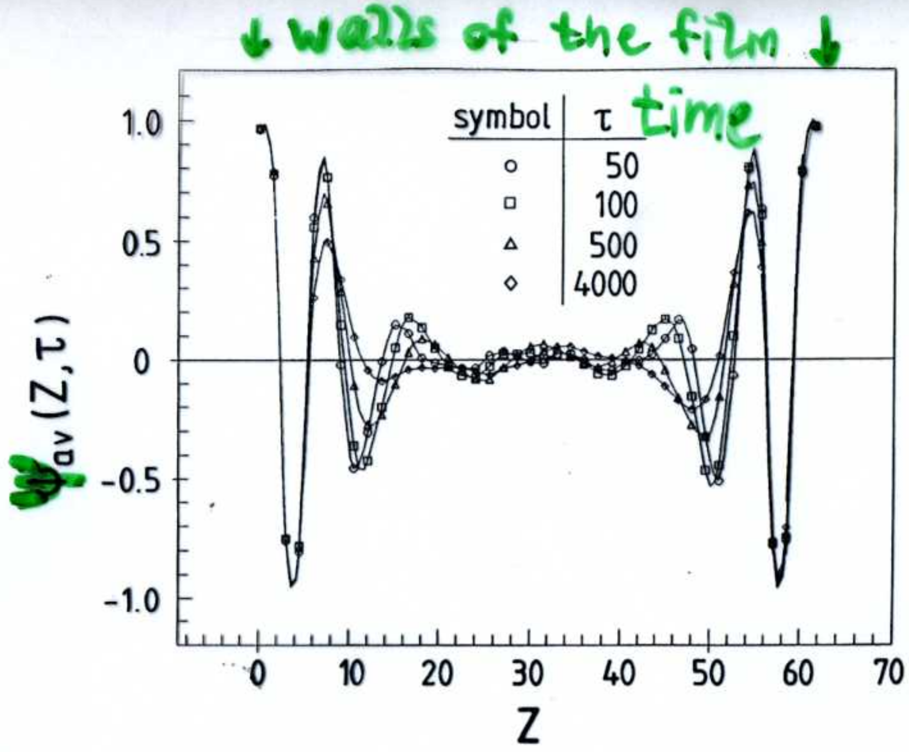
? MONTE CARLO ?

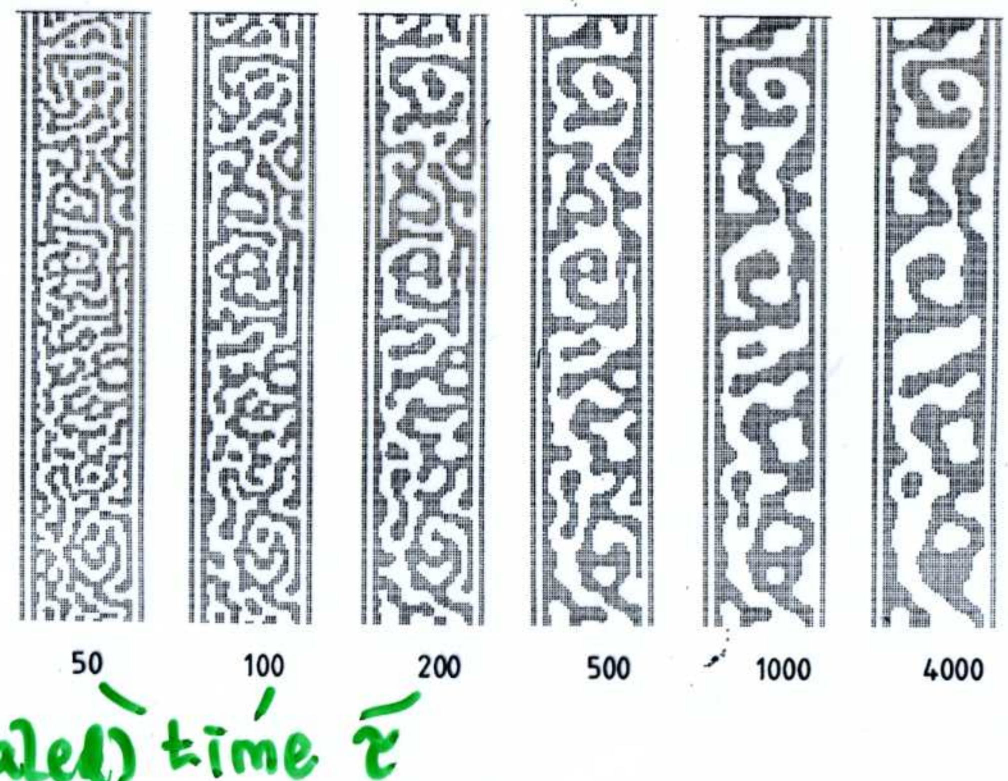
waste of effort, thermal fluctuations unimportant at late stages (and deep quenches)

S. Puri + K. Binder (1992, 1994, ...):
numerical solution of time-dependent GINZBURG-LANDAU equation with CONSERVED ORDER PARAMETER ("Model B")

NEEDS PROPER BOUNDARY CONDITIONS AT THE SURFACES !

$$\frac{\partial \psi(\vec{\rho}, z, \tau)}{\partial \tau} = -\nabla^2 \left\{ \psi - \psi^3 + \frac{\nabla^2 \psi}{2} \right\}$$





Derivation of boundary conditions for G-L treatment of surface-directed S D

"pedestrian approach": Molecular field theory for Kawasaki kinetic Ising model with surface ⟶ continuum approximation (differences → differentials)

K.B. + H.L. Frisch (1991)

simple but tedious → more elegant alternatives

SYMMETRY ARGUMENTS etc. Diehl and Janssen (1992)

→ ADVANTAGE: Lattice mean-field treatment of the Kawasaki spin exchange model can be solved numerically also at low temperatures

⇒ quick and efficient alternative to Monte Carlo simulation

Molecular Field Theory for the Kawasaki kinetic Ising model in a thin film

lattice site $i \hat{=} (n, \vec{\rho})$ $\quad \langle S_i \rangle_T = m_n(\vec{\rho})$ equilibrium

$\langle S_i(t) \rangle_T = m_n(\vec{\rho}, t)$ nonequilibrium relaxation

EQUILIBRIUM:

$$F = \sum_{n=1}^{D} (E_n - TS_n), \quad S_n / k_B T = \sum_{\vec{\rho}} \left\{ \frac{1+m_n(\vec{\rho})}{2} \ln \frac{1+m_n(\vec{\rho})}{2} + \frac{1-m_n(\rho)}{2} \ln \frac{1-m_n(\rho)}{2} \right\},$$

energy: $S_i \to m_n(\rho)$ in the Hamiltonian

$$\left(\frac{\partial F}{\partial m_n(\vec{\rho})} \right)_{T,H,H_1} = 0 \Rightarrow m_n(\rho) = \tanh \left\{ \frac{J}{k_B T} \left[m_{n-1}(\vec{\rho}) + m_{n+1}(\vec{\rho}) + \sum_{\Delta \vec{\rho}} m_n(\vec{\rho} + \Delta \vec{\rho}) \right] \right\}$$

$2 \le n \le D-1$

$m_1(\vec{\rho}) = \ldots, \; m_D(\vec{\rho}) = \ldots$

Nonequilibrium: Kawasaki spin-exchange kinetic Ising model

transition probability (Glauber) $\uparrow\downarrow \Leftrightarrow \downarrow\uparrow$

$$W(S_i \to S_j, S_j \to S_i) = \frac{1}{2\tau_s}\left[1 - \tanh(\delta \mathcal{H}/2k_BT)\right]$$

$\Rightarrow$ coupled set of nonlinear kinetic equations for the local magnetizations $m_n(\vec{\rho},t)$

$$2\tau_s \frac{d}{dt} m_n(\vec{\rho},t) = \ldots\ldots, \quad 3 \leq n \leq D-2$$

$$2\tau_s \frac{d}{dt} m_1(\vec{\rho},t) = \ldots\ldots, \quad \tau_s \frac{d}{dt} m_D(\vec{\rho},t) = \ldots\ldots$$

(boundary layers)

$$2\tau_s \frac{d}{dt} m_2(\vec{\rho},t) = \ldots\ldots, \quad 2\tau_s \frac{d}{dt} m_{D-1}(\vec{\rho},t) = \ldots\ldots$$

(layers adjacent to a boundary can exchange spin with boundary) example: n=1

only 5 spins available for exchange

$$
\begin{aligned}
2\tau_s \frac{d}{dt} m_1(\vec{\rho},t) = & -5\, m_1(\vec{\rho},t) + m_2(\vec{\rho},t) + \sum_{\Delta\vec{\rho}} m_1(\vec{\rho}+\Delta\vec{\rho},t) \\
& + \left[1 - m_1(\vec{\rho},t)\, m_2(\vec{\rho},t)\right] \tanh \frac{J}{k_B T} \Big[m_2(\vec{\rho},t) + \frac{H_1}{J} \\
& \quad + \frac{J_s}{J} \sum_{\Delta\vec{\rho}} m_1(\vec{\rho}+\Delta\vec{\rho},t) - m_3(\vec{\rho},t) - m_1(\vec{\rho},t) - \sum_{\Delta\vec{\rho}} m_2(\vec{\rho}+\Delta\vec{\rho},t) \Big] \\
& + \sum_{\Delta\vec{\rho}} \left[1 - m_1(\vec{\rho},t)\, m_1(\vec{\rho}+\Delta\vec{\rho},t)\right] \tanh \frac{J}{k_B T} \Big[m_2(\vec{\rho},t) \\
& \quad + \frac{J_s}{J} \sum_{\Delta\vec{\rho}'} m_1(\vec{\rho}+\Delta\vec{\rho}',t) - m_2(\vec{\rho}+\Delta\vec{\rho},t) \\
& \quad - \frac{J_s}{J} \sum_{\Delta\vec{\rho}'} m_1(\vec{\rho}+\Delta\vec{\rho}'+\Delta\vec{\rho},t) \Big]
\end{aligned}
$$

differences of local effective fields enter

Derivation of boundary conditions for the G-L differential equation: DIFFERENCES IN COORDINATES → DIFFERENTIALS

$$m_{n\pm1}(\vec{\rho},t) = m_n(\vec{\rho},t) \pm \frac{\partial m_n}{\partial n}(\vec{\rho}) + \frac{1}{2}\frac{\partial^2 m_n(\vec{\rho},t)}{\partial n^2} \pm \frac{1}{6}\frac{\partial^3 m_n(\vec{\rho},t)}{\partial n^3} + \frac{1}{24}\frac{\partial^4 m_n(\vec{\rho},t)}{\partial n^4}$$

$$m_n(\vec{\rho}+\Delta\vec{\rho},t) = m_n(\vec{\rho},t) + (\Delta\vec{\rho}\cdot\nabla_{\parallel})\, m_n(\vec{\rho},t) + \ldots\ldots$$

straightforward algebra ⇒ $(z = na)$, $\Phi(\vec{\rho},z,t) = m_n(\vec{\rho},t)$

$$2\tau_s \frac{\partial}{\partial t}\Phi(\vec{\rho},z=0,t) = \frac{H_1}{T} + \frac{J}{T}\left(4\frac{J_s}{J}-5\right)\Phi(\vec{\rho},z=0,t) + \frac{J}{T}\frac{\partial\Phi(\vec{\rho},z,t)}{\partial z}\Bigg|_{z=0}$$

(leading order near T_{cb} only: $\xi \gg 1$!)

$$\frac{\partial}{\partial z}\left\{\left(\frac{T_{cb}}{T}-1\right) - \frac{1}{3}\left[\Phi(\vec{\rho},z,t)\right]^3 + \frac{J}{T}\frac{\partial^2}{\partial z^2}\left[\Phi(\vec{\rho},z,t)\right]\right\}_{z=0} = 0$$

no flux across boundary

derivation only justifiable if concentration variations are SLOW ON SCALE OF THE LATTICE SPACING a

$\Rightarrow$ correlation length ξ at coexistence large

$$\xi^2 = \frac{a^2}{\dfrac{k_B T/J}{1-m_b^2} - \dfrac{k_B T_{cb}}{J}}$$

$$\approx \frac{a^2/12}{1-T/T_{cb}}$$ near $T_{cb} = 6J/k_B$

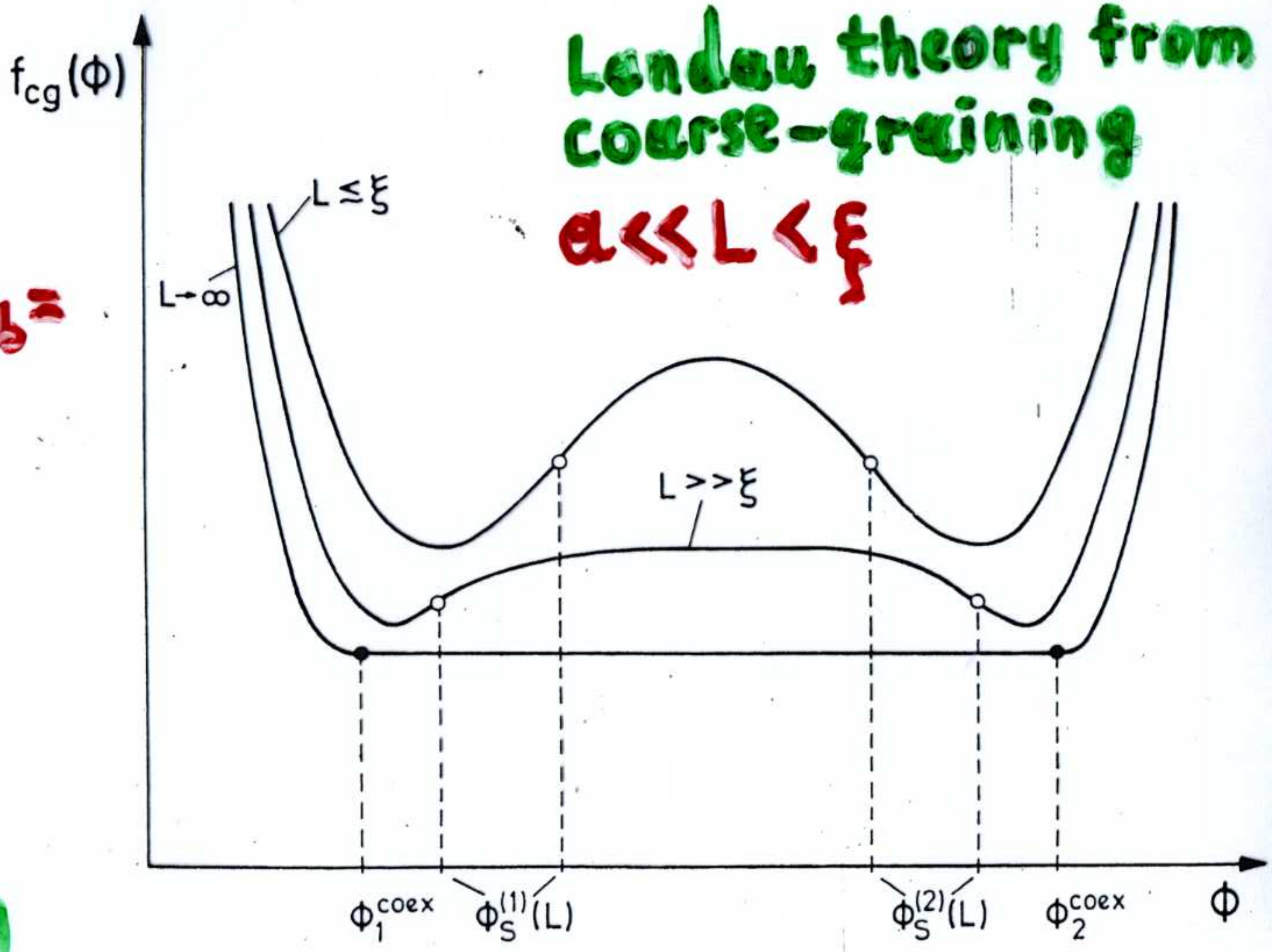
$\xi = a$: $T = 5.57\ J/k_B$

$\xi = 2a$: $T = 5.875\ J/k_B$

$T/T_{cb} \approx 0.98$!

Landau theory from coarse-graining

$a \ll L < \xi$



L = coarse-graining cell size

S.K. DAS, J. HORBACH, K.B. (2008)

numerical solution of nonlinear MF lattice model

$t=0: T=\infty$

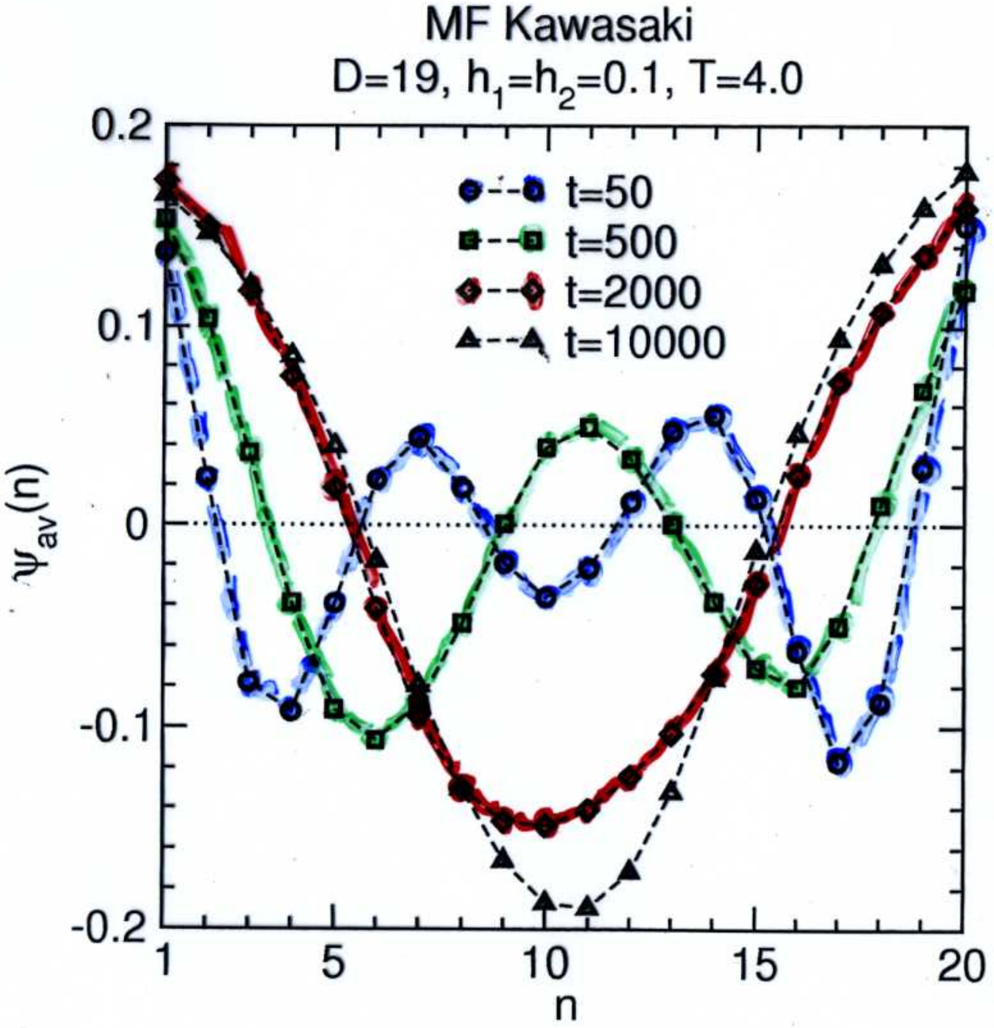
$m_n(\vec{\rho}, t=0) = \pm 1$ (random)

quench to $T/T_{cb} = 2/3$

$L_x = L_y = 128$

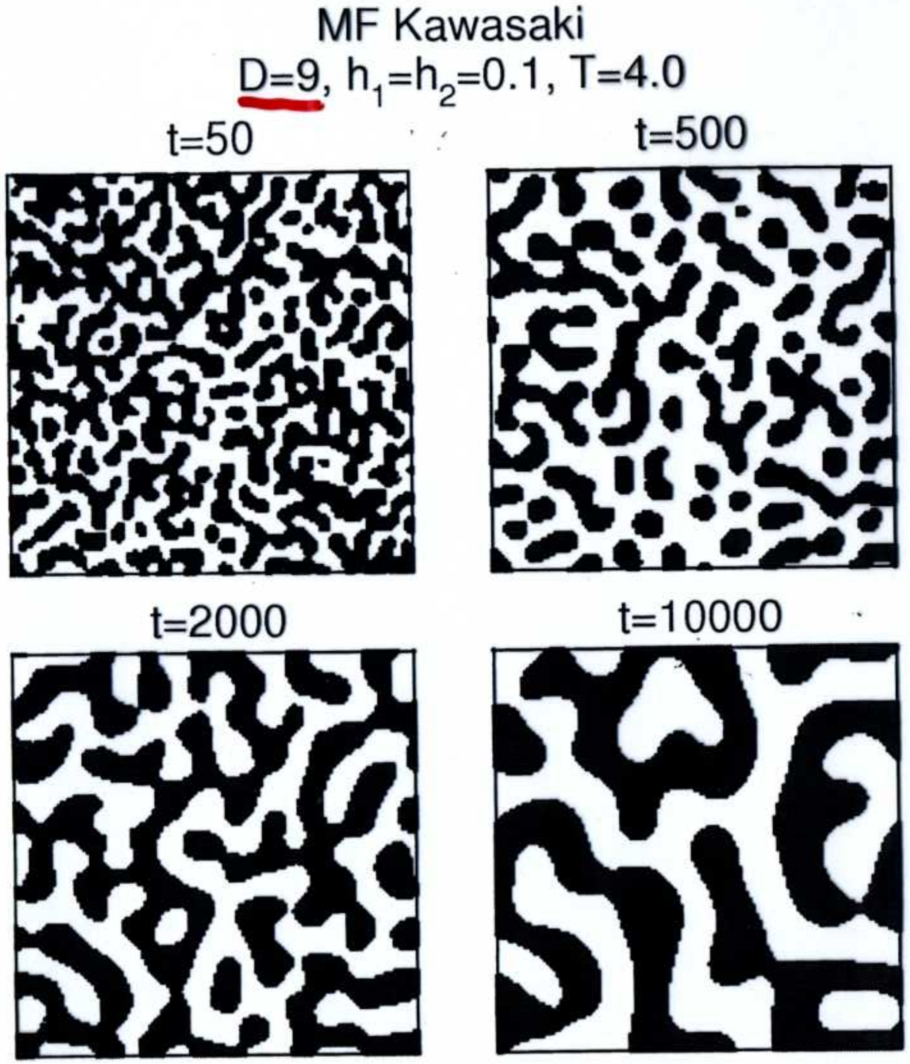
$a \equiv 1$

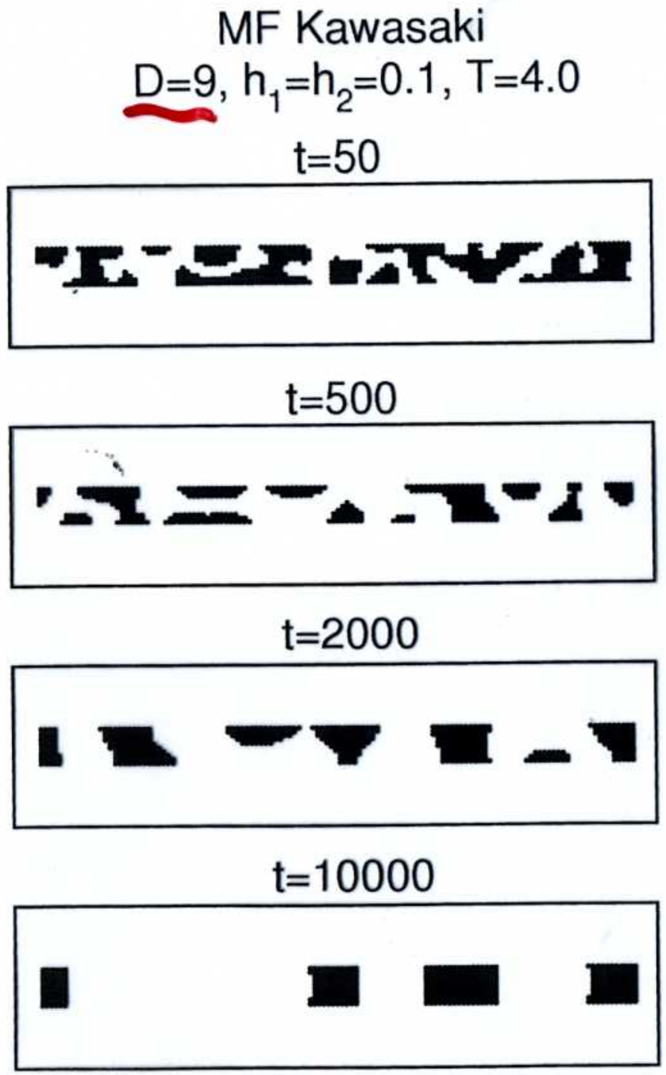
$J/k_B = 1$



LATTICE MOLECULAR FIELD THEORY : SNAPSHOT PICTURES

cross section parallel to the walls

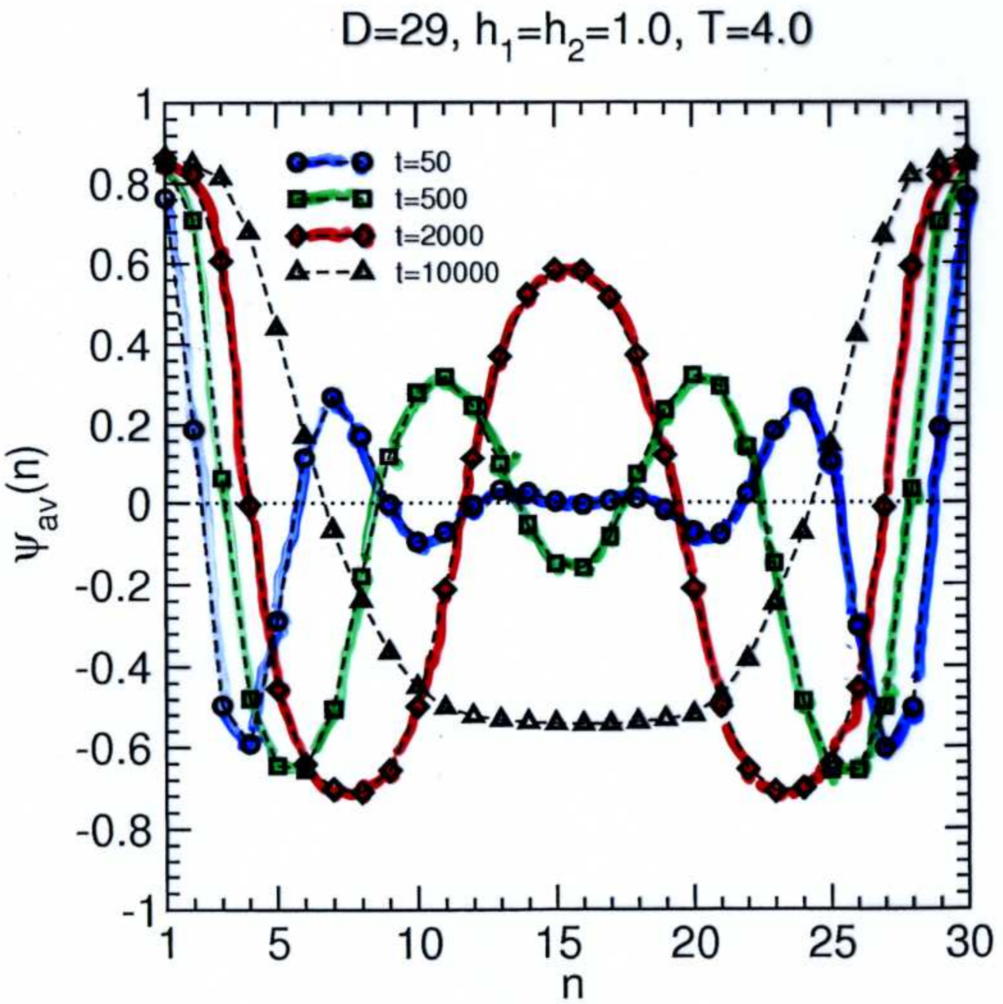


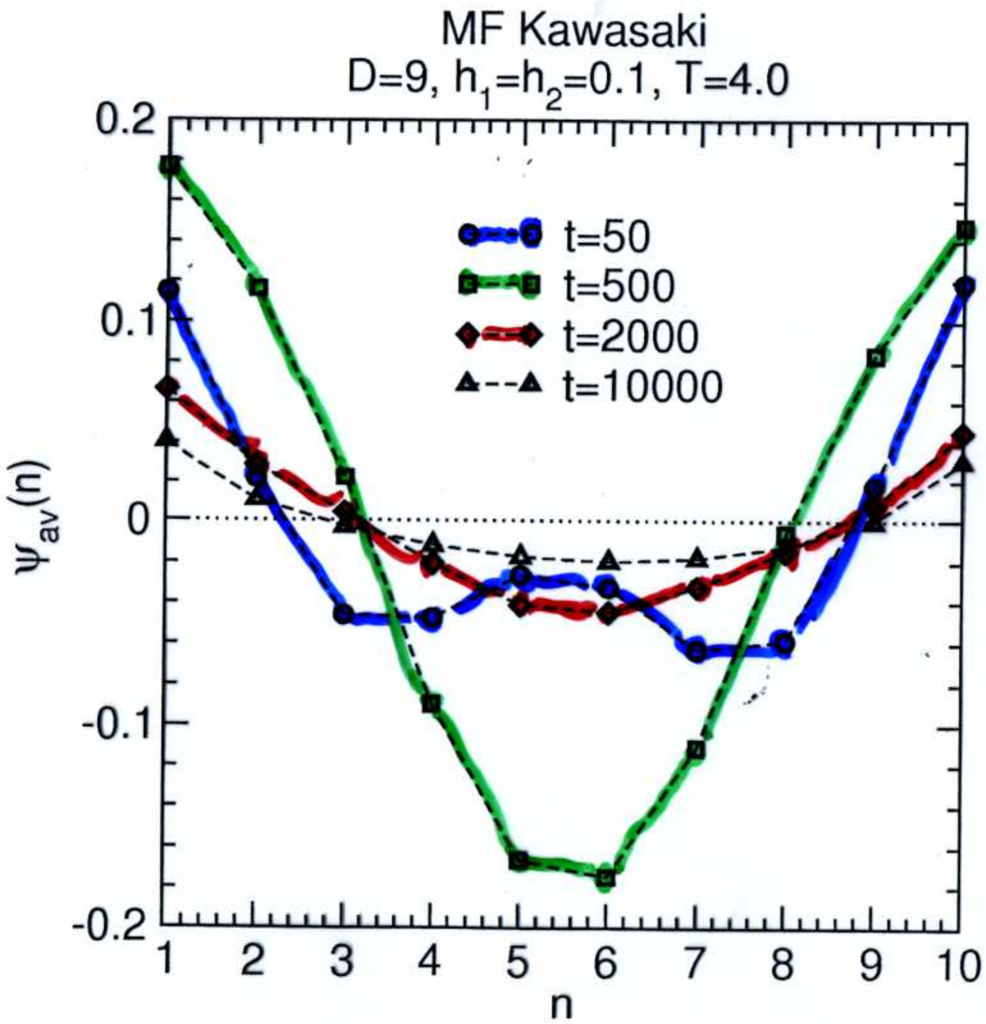


in the middle of the thin film

$L_x = L_y = 128$

$T/T_{cb} = 2/3: \ \xi \approx \frac{1}{3}$(lattice spacings) !



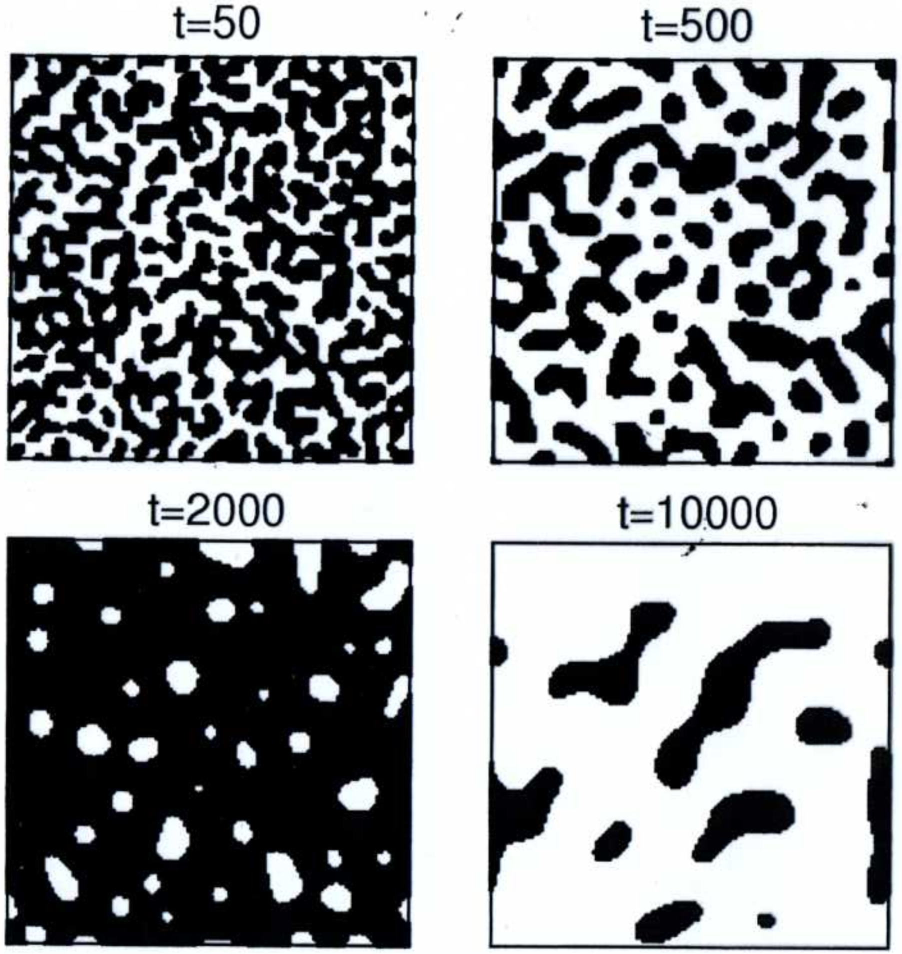


rapid concentration variations accurately resolved

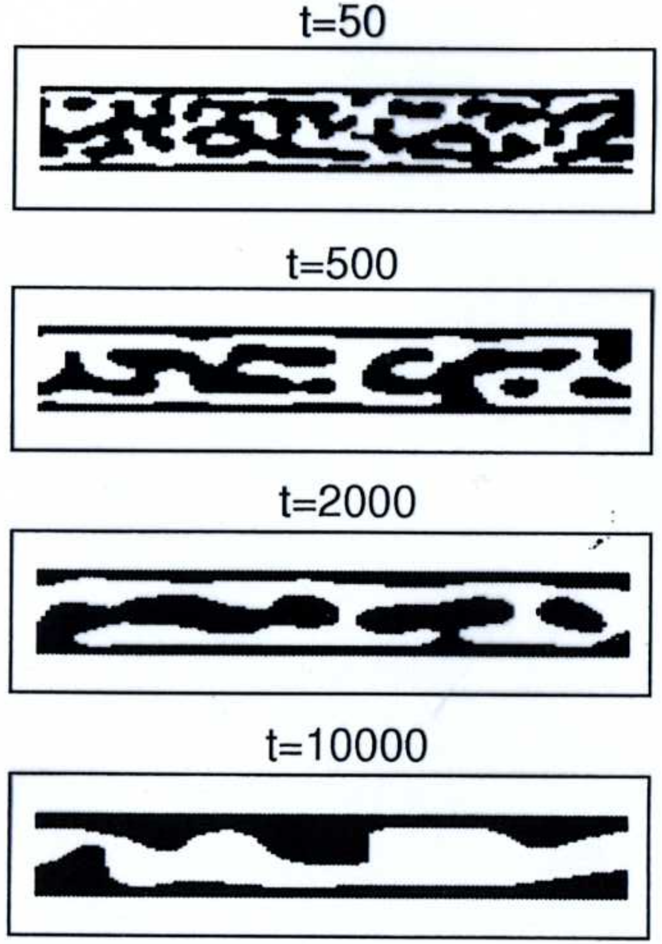
LATTICE MOLECULAR FIELD THEORY: SNAPSHOT PICTURES

cross section parallel to the walls
in the middle of the thin film

MF Kawasaki
D=29, $h_1=h_2=1.0$, T=4.0

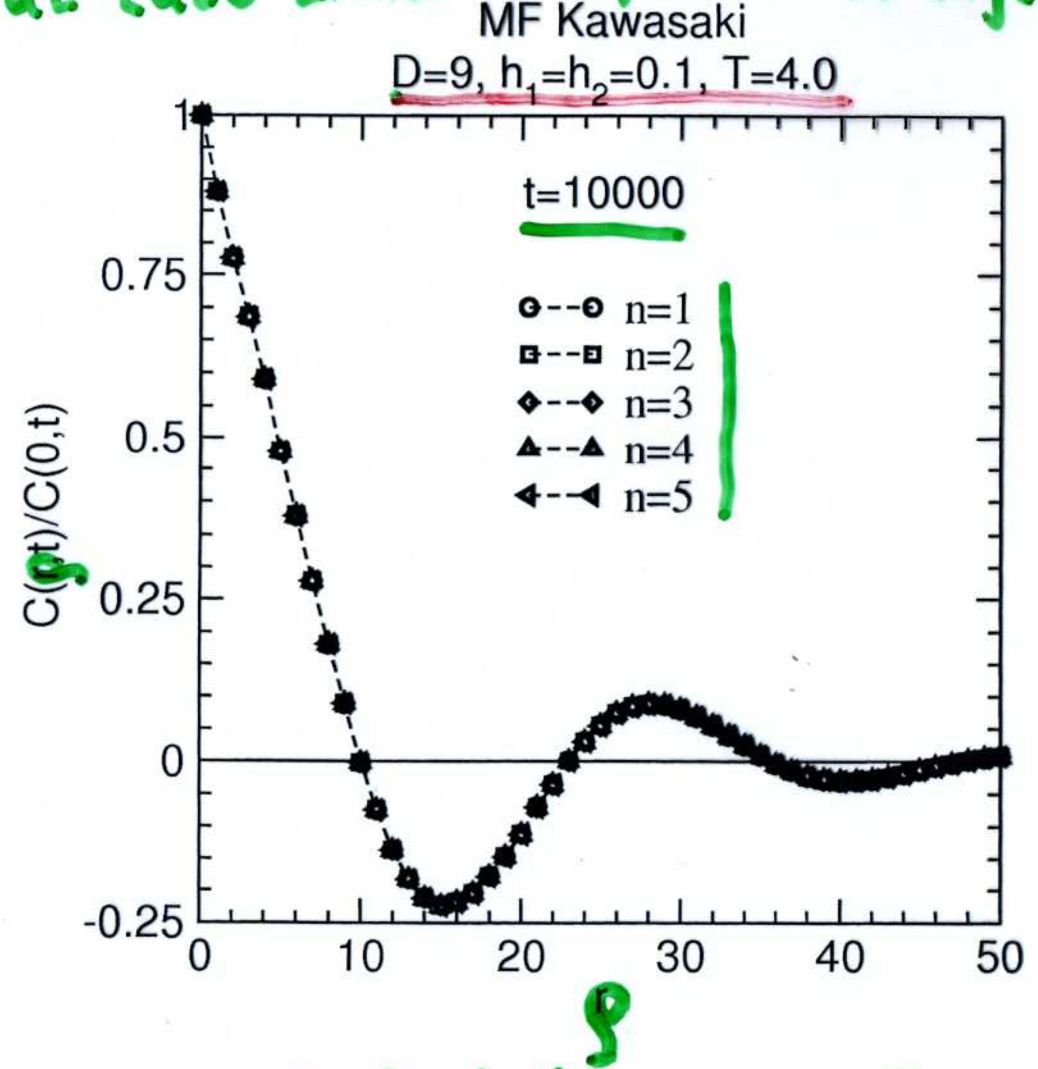


MF Kawasaki
D=29, $h_1=h_2=1.0$, T=4.0

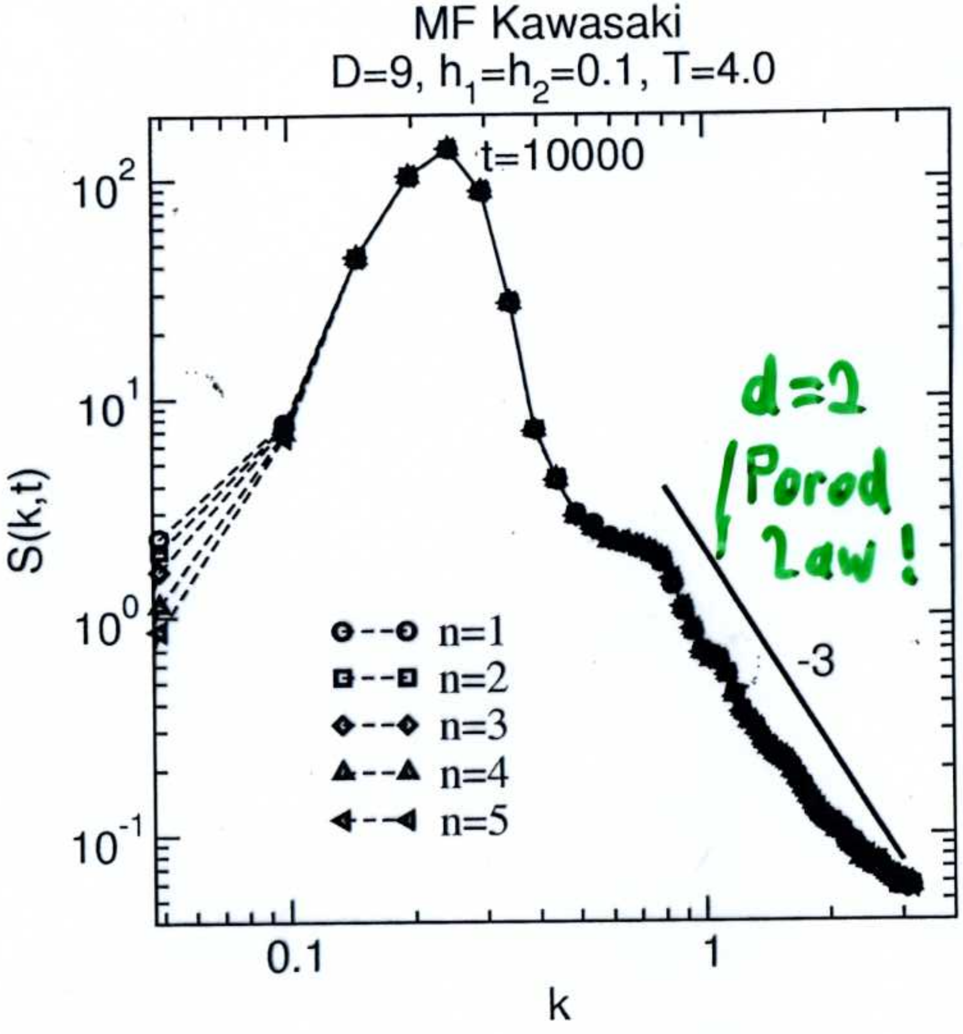


EQUAL-TIME STRUCTURE FACTOR

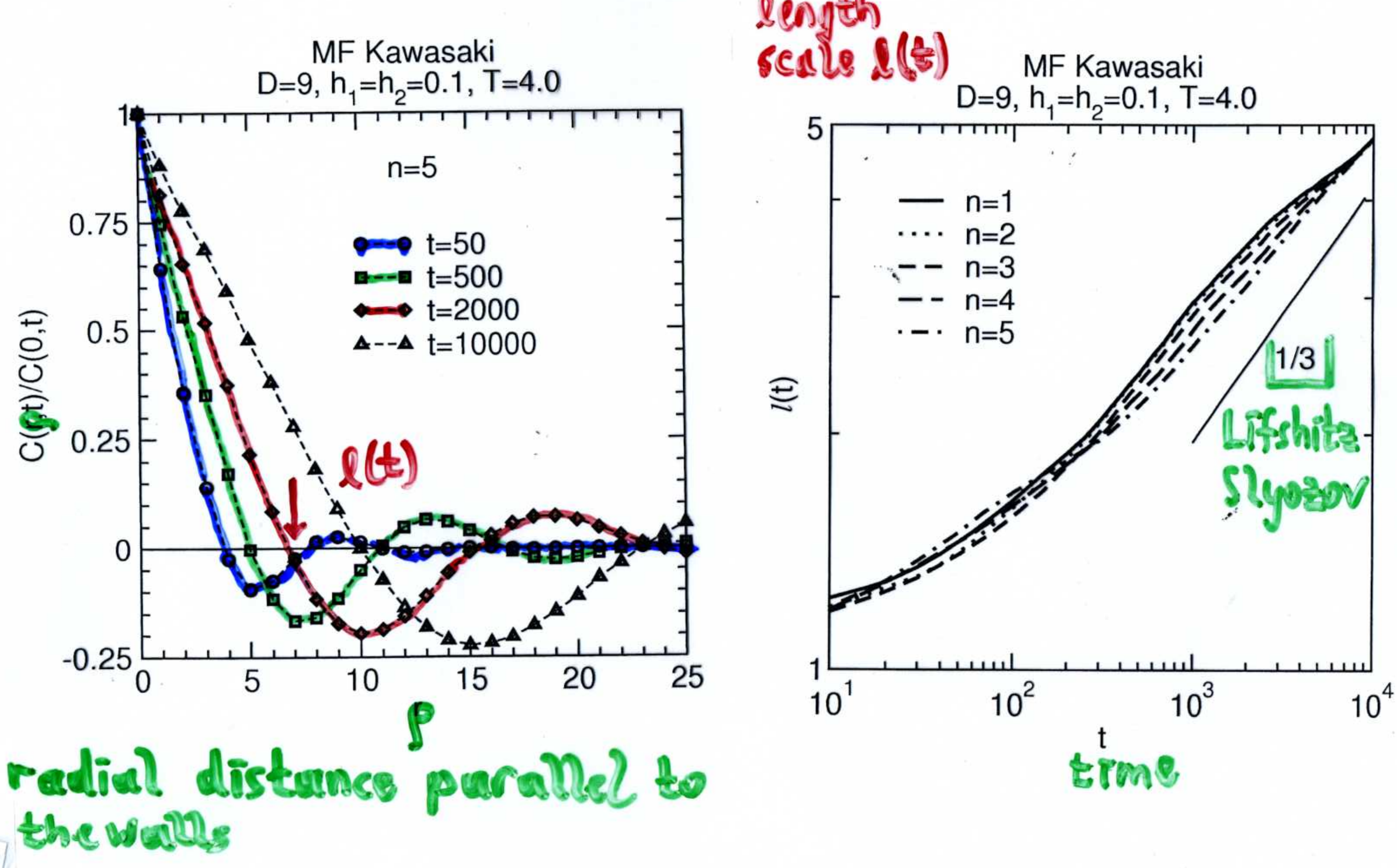
Correlation function in radial direction at late times: independent of layer index n



radial distance parallel to the walls

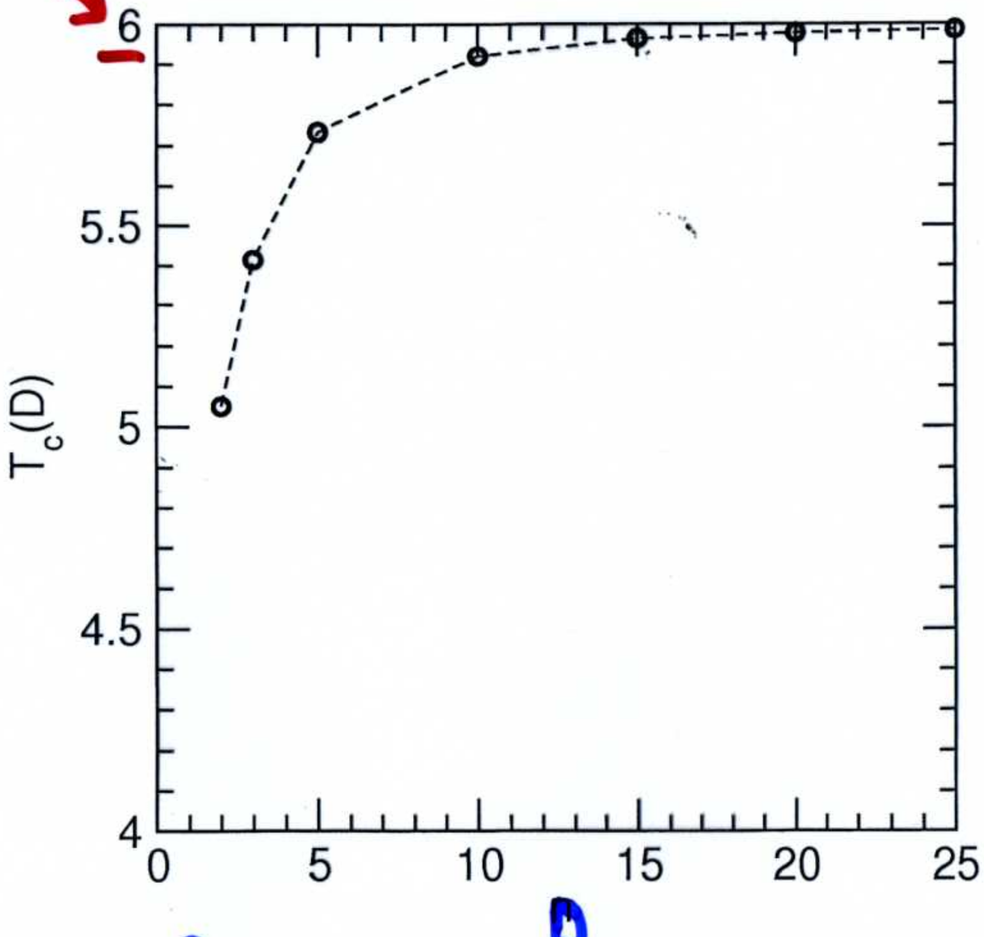


$T/T_{cb} = 2/3 \quad \xi \approx 1/3$



MF Kawasaki
D=9, h1=h2=0.1, T=4.0
n=5
t=50
t=500
t=2000
t=10000
C(ρ,t)/C(0,t)
l(t)
ρ
radial distance parallel to the walls
length scale l(t)
MF Kawasaki
D=9, h1=h2=0.1, T=4.0
n=1
n=2
n=3
n=4
n=5
1/3
Lifshitz Slyozov
l(t)
t
time

COMPARISON BETWEEN GINZBURG-LANDAU THEORY AND LATTICE MOLECULAR FIELD THEORY CLOSE TO T_{cb}



also $D \gg \xi$ required: SHIFT of T_c with film thickness!

$\xi = 2$:
$T = 5.875$
$(T/T_{cb} \approx 0.98)$

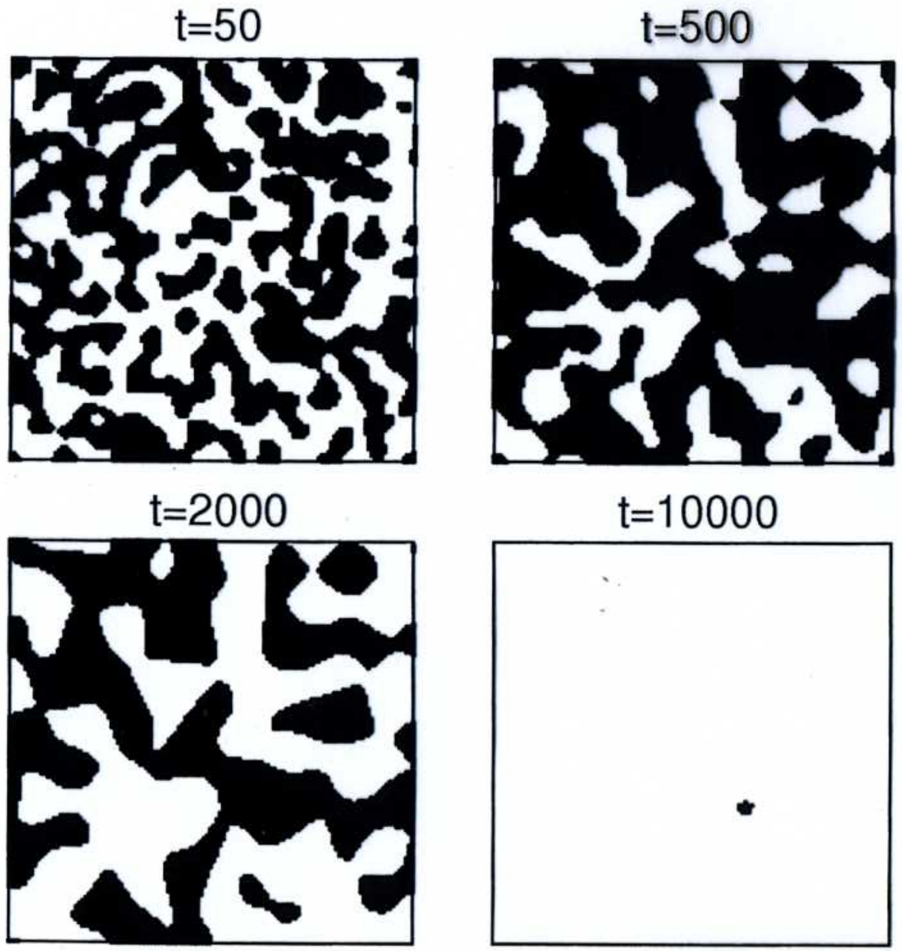
larger values of ξ would fall in the one-phase region of our thin films with $D+1 = 10, 20, 30$ lattice planes...

MFT: $T_{cb} - T_c(D) \propto D^{-2}$

Comparison between lattice and continuum models: SNAPSHOTS parallel to the walls

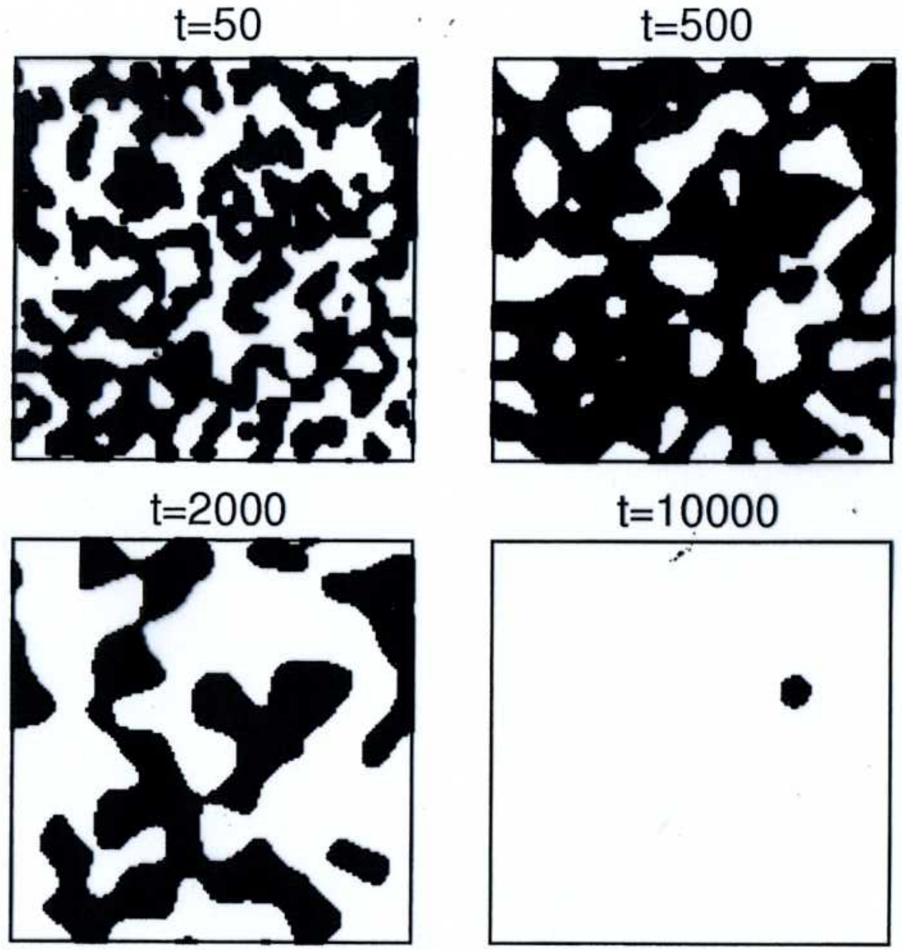
MF Kawasaki

$D=29$, $h_1=h_2=0.1$, $T=5.875$



GL model

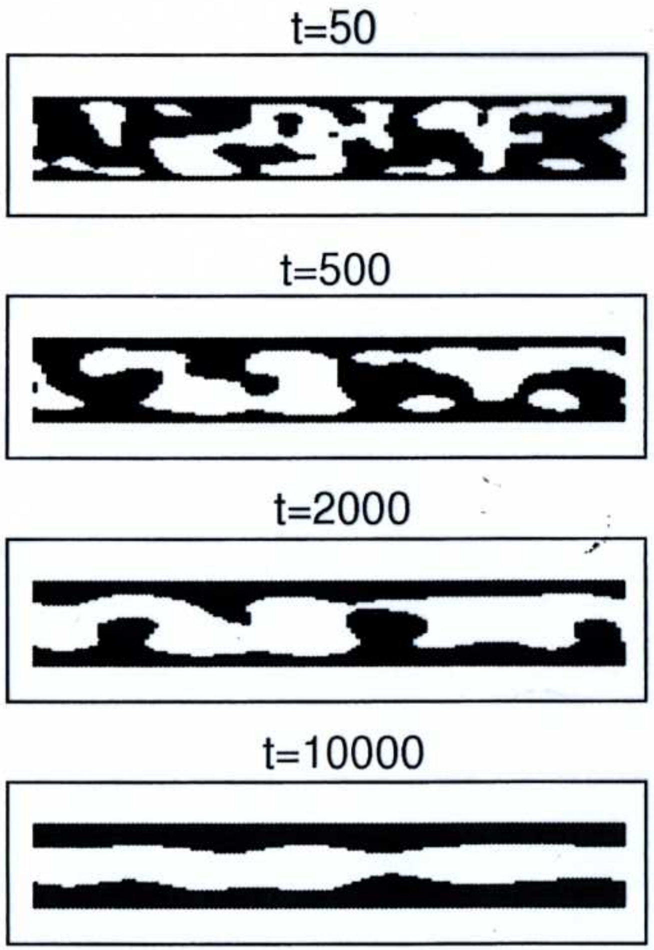
$D=29$, $h_1=h_2=0.1$, $T=5.875$



Comparison between lattice and continuum models
SNAPSHOTS of cross sections perpendicular to the walls

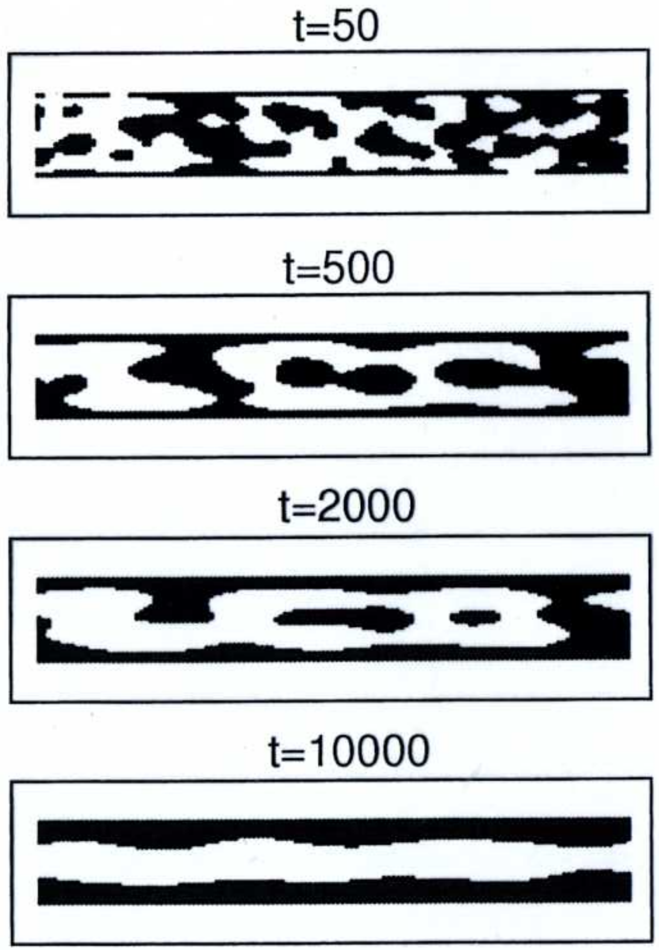
GL model

D=29, $h_1=h_2=0.1$, T=5.875



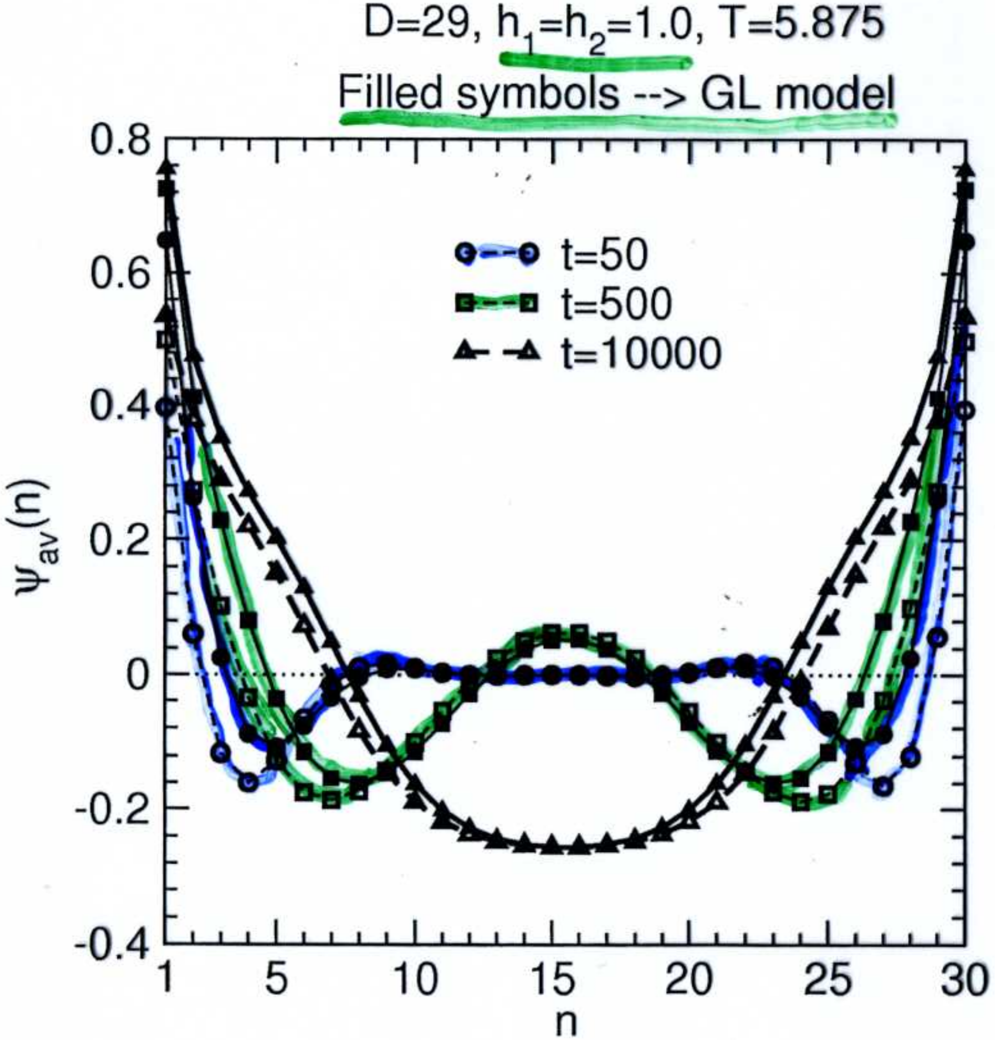
MF Kawasaki

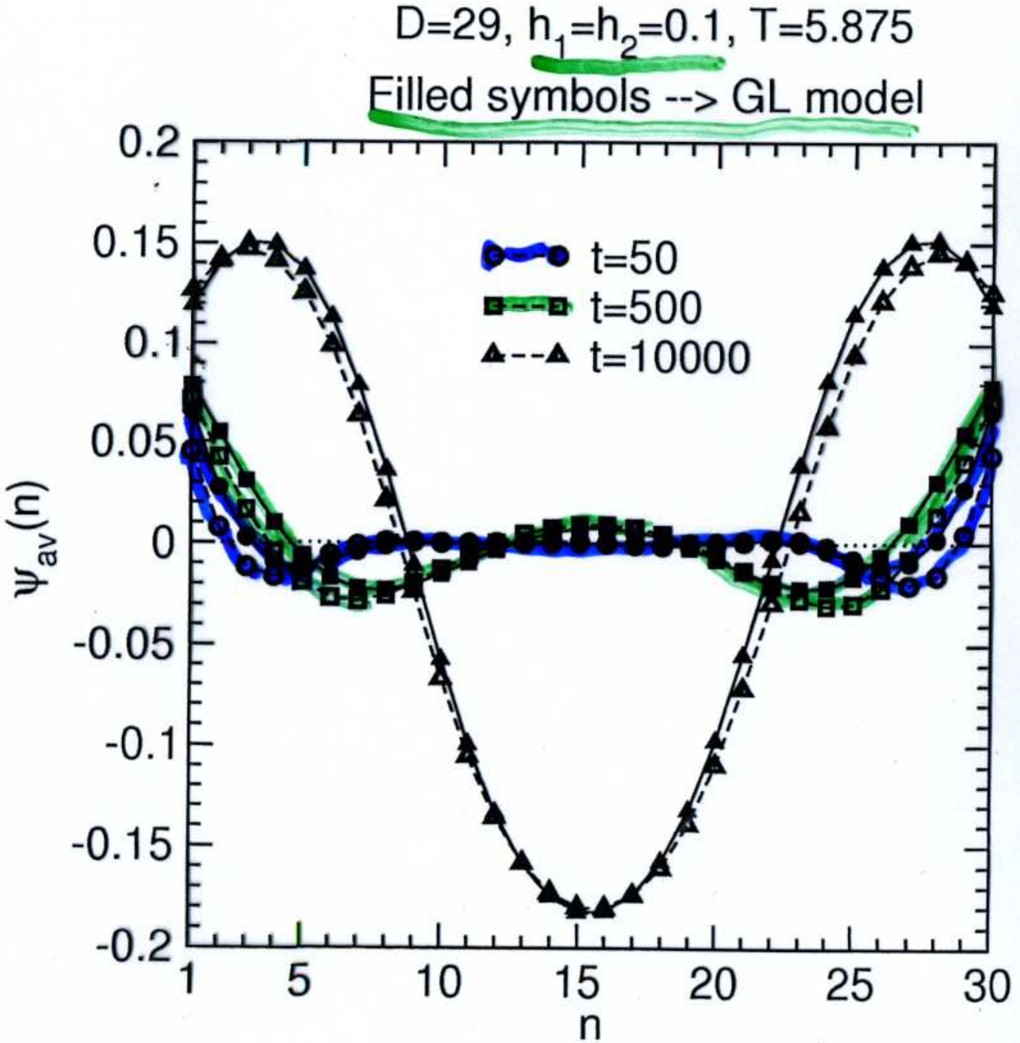
D=29, $h_1=h_2=0.1$, T=5.875



COMPARISON between LATTICE and CONTINUUM models

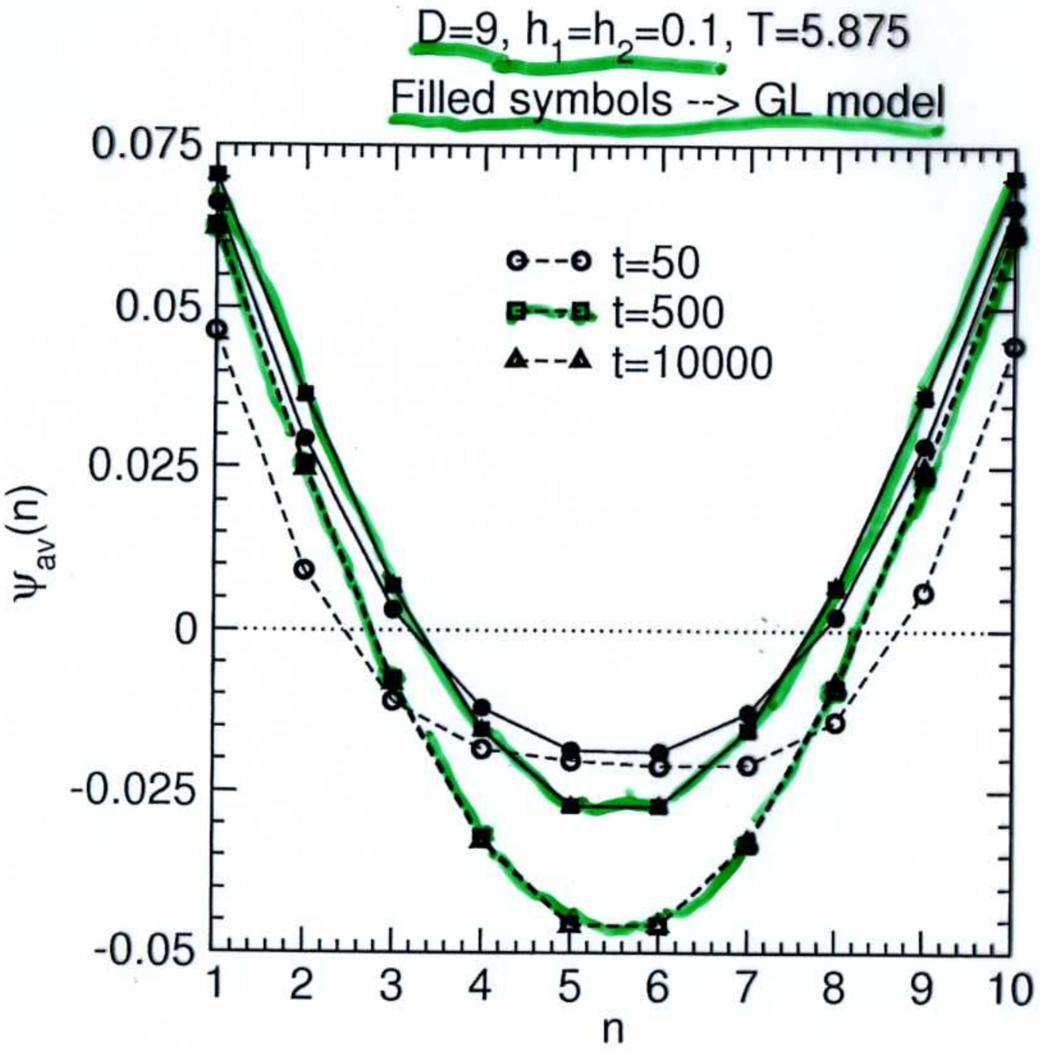
Concentration profiles perpendicular to the walls

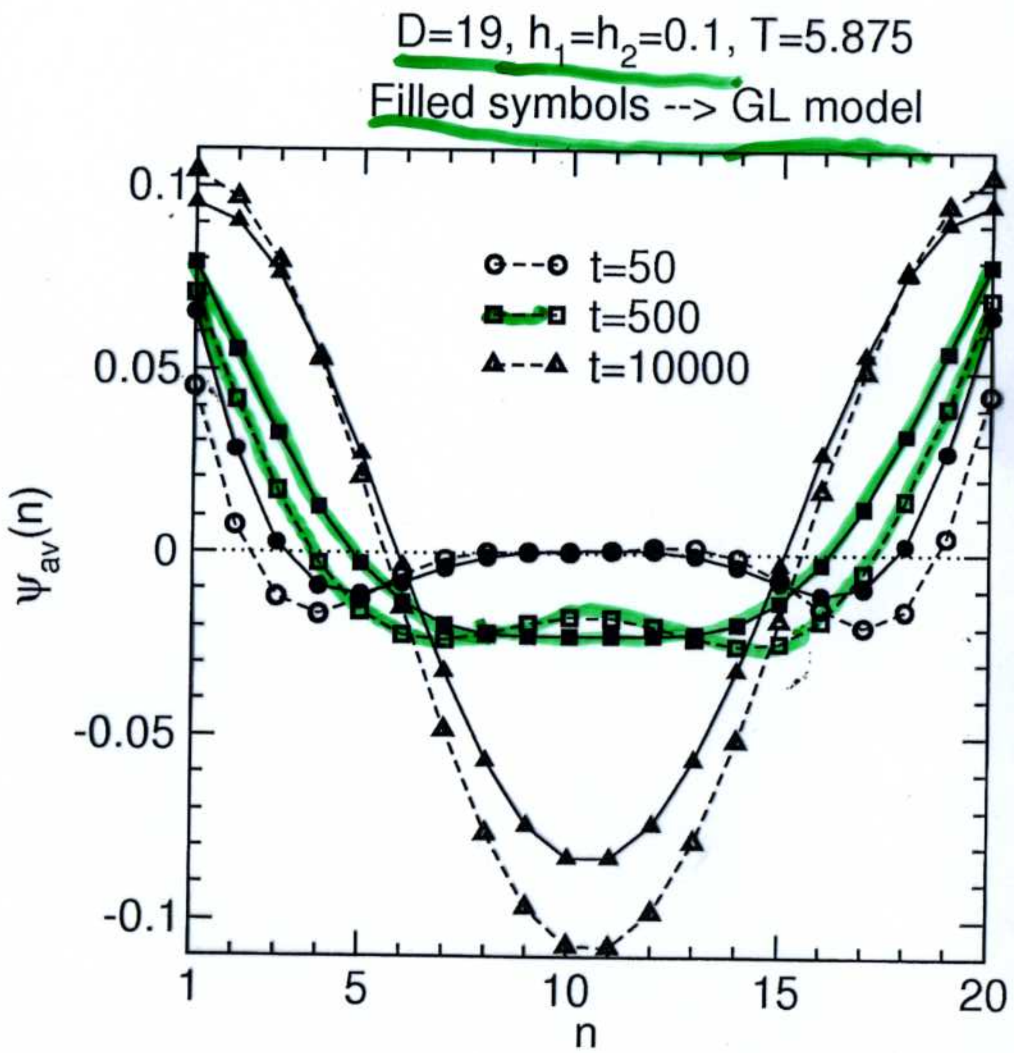




COMPARISON between LATTICE and CONTINUUM models

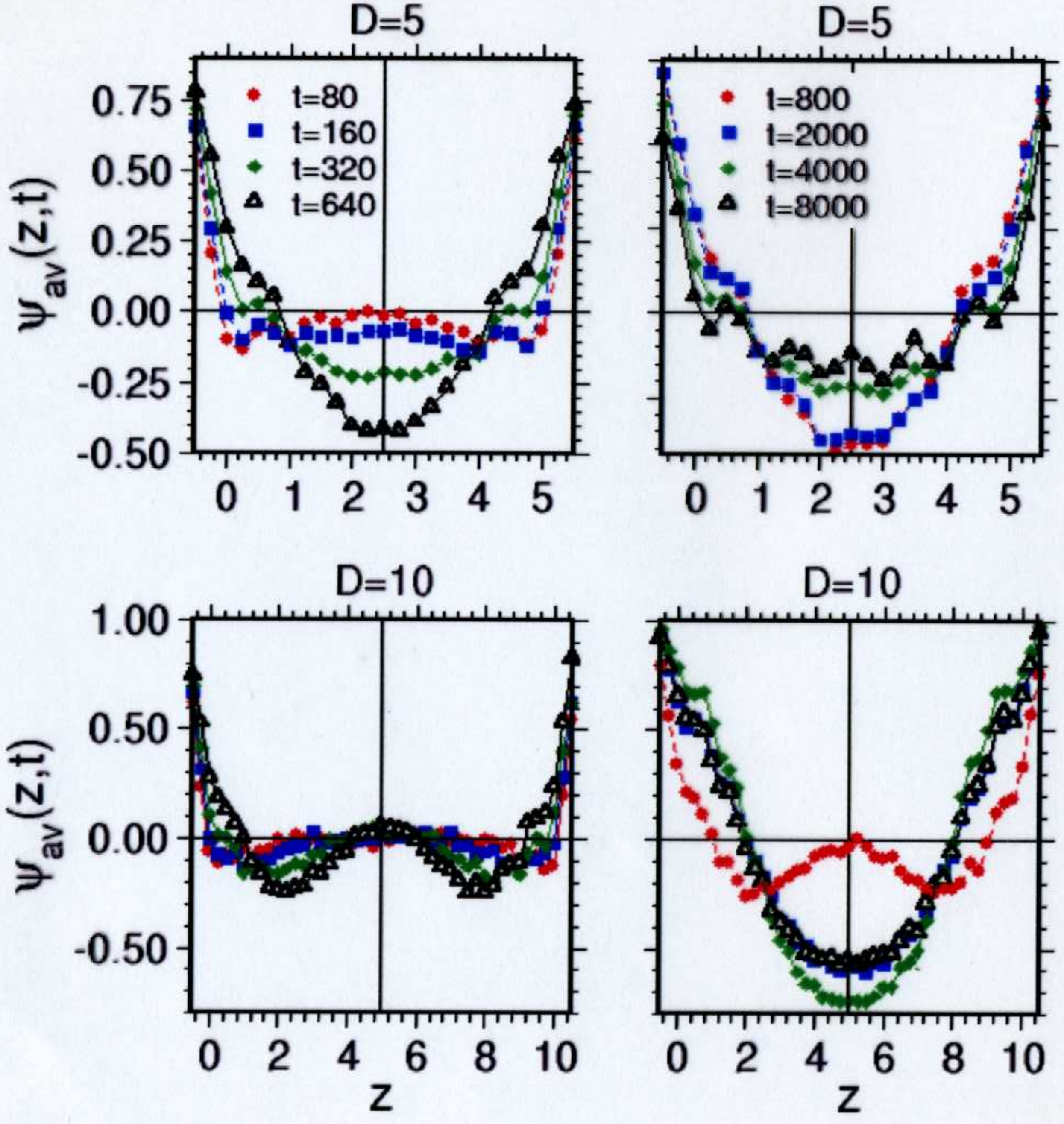
CONCENTRATION PROFILES perpendicular to the walls





D not large: results qualitatively similar, but not a perfect agreement

Order parameter profiles (MD)



binary symmetric Lennard-Jones mixture

$\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon = 1$

$\varepsilon_{AB} = \varepsilon/2$; $\sigma = 1$

$T_c = 1.638$

(density $\rho = 1$)

quench: $T = 5 \rightarrow 1.1$

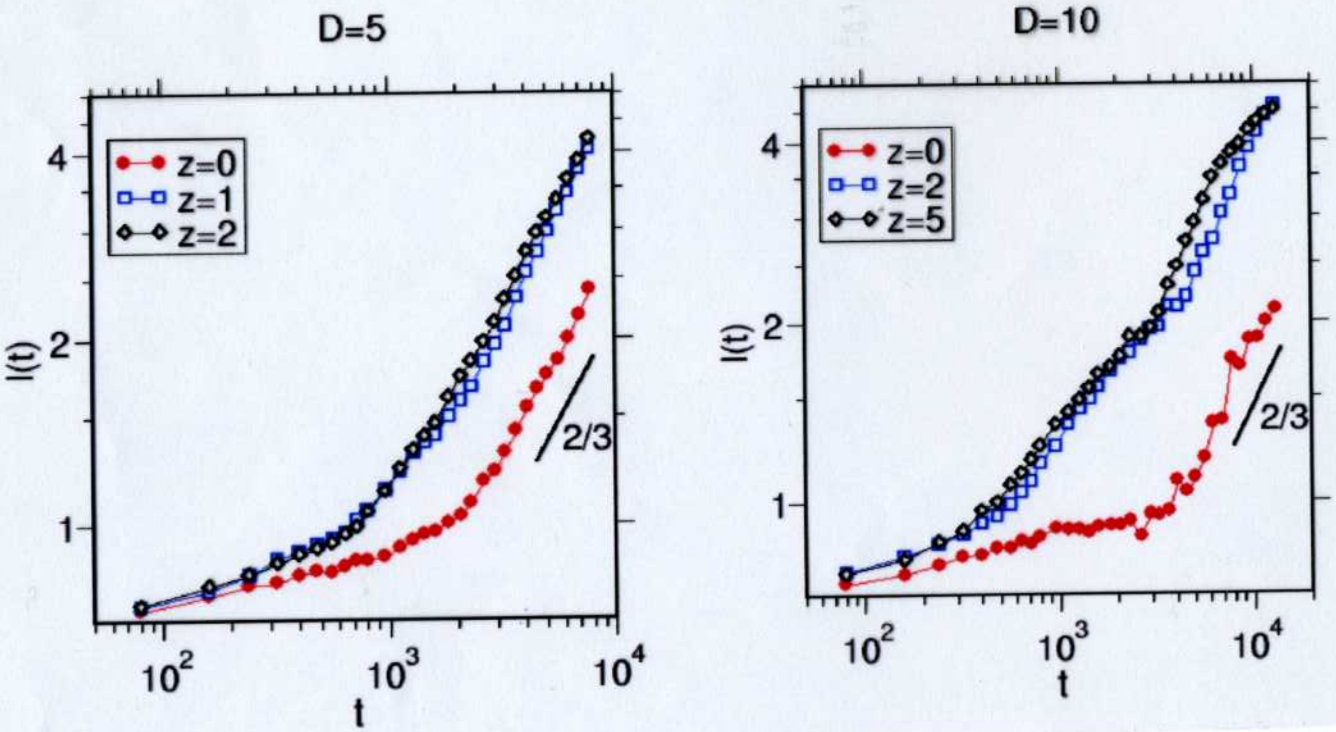
(equilibrium $\langle\psi\rangle \approx \pm 1$, $\xi = 1$)

time unit

$\tau = (m\sigma^2/48\varepsilon)^{1/2}$

Molecular Dynamics simulation

Domain length scale



fluid

binary symmetric Lennard-Jones mixture

$\ell(t) \propto t^{2/3}$?

effect due to hydrodynamic interactions?

CONCLUSIONS

- LATTICE MODEL FOR SPINODAL DECOMPOSITION OF SOLID MIXTURES WITH SURFACES DERIVED FROM KAWASAKI KINETIC ISING MODEL IN MEAN FIELD
  → faster than MONTE CARLO
  → boundary conditions for GINZBURG-LANDAU
  → GL theory quantitatively equivalent to lattice mean field theory only for $T \geq 0.98\, T_{cb}$
  → Lattice MFT for Kawasaki model useful for full temperature range, computationally as convenient as discretization of GL theory; generalization to realistic models of solid binary alloys possible
- FLUID BINARY MIXTURES BEHAVE DIFFERENT: MD